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QUANTITATIVE INORGANIC ANALYSIS

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A TEXT BOOK OF

QUALITATIVE CHEMICAL ANALYSIS

With Illustrations

" An excellent guide to the student from the early stages in his career up to the Honours courses."—*Nature.*

A TEXT-BOOK OF

QUANTITATIVE INORGANIC ANALYSIS

THEORY AND PRACTICE

BY

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With Plates and Diagrams

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PREFACE

In writing this book, the author had as his primary object the provision of a complete up-to-date text book of quantitative inorganic analysis, both theory and practice, at a moderate price to meet the requirements of University and College students of all grades. It is believed that the material contained therein is sufficiently comprehensive to cover the syllabuses of all examinations in which quantitative inorganic analysis plays a part. The elementary student has been provided for, and those sections devoted to his needs have been treated in considerable detail. The volume should therefore be of value to the student throughout the whole of his career. The book will be suitable *inter alia* for students preparing for the various Intermediate B.Sc. and Higher School Certificate Examinations, the Ordinary and Higher National Certificates in Chemistry, the Honours and Special B.Sc. of the Universities, the Associateship of the Institute of Chemistry, and other Examinations of equivalent standard. It is hoped, also, that the wide range of subjects discussed within its covers will result in the volume having a special appeal to practising analytical chemists and to all those workers in industry and research who have occasion to utilise methods of inorganic quantitative analysis.

The kind reception accorded to the author's *Text Book of Qualitative Chemical Analysis* by teachers and reviewers seems to indicate that the general arrangement of that book has met with approval. The companion volume on *Quantitative Inorganic Analysis* follows essentially similar lines. Chapter I is devoted to the theoretical basis of quantitative inorganic analysis, Chapter II to the experimental technique of quantitative analysis, Chapter III to volumetric analysis, Chapter IV to gravimetric analysis (including electro-analysis), Chapter V to colorimetric analysis and Chapter VI to gas analysis ; a comprehensive Appendix has been added, which contains much useful matter for the practising analytical chemist. The experimental side is based essentially upon the writer's experience with large classes of students of various grades. Most of the determinations have been tested out in the laboratory in collaboration with the author's colleagues and senior students, and in some cases this has resulted in slight modifications of the details given by the original authors. Particular emphasis has been laid upon recent developments in experimental technique. Frequently the source of certain apparatus or chemicals has been given in the text : this is not intended to convey the impression that these materials cannot be obtained from other sources, but merely to indicate that the author's own experience is confined to the particular products mentioned.

The ground covered by the book can best be judged by perusal of the Table of Contents. An attempt has been made to strike a balance between the classical and modern procedures, and to present the subject of analytical chemistry as it is to-day. The theoretical aspect has been stressed throughout, and numerous cross-references are given to Chapter I (the theoretical basis of quantitative inorganic analysis).

No references to the original literature are given in the text. This is because the introduction of such references would have considerably increased the size and therefore the price of the book. However, a discussion on the literature of analytical chemistry is given in the Appendix (Section **A, 3**). With the aid of the various volumes mentioned therein—which should be available in all libraries of analytical chemistry—and the Collective Indexes of Chemical Abstracts or of British Chemical Abstracts, little difficulty will, in general, be experienced in finding the original sources of most of the determinations described in the book.

In the preparation of this volume, the author has utilised pertinent material wherever it was to be found. While it is impossible to acknowledge every source individually (see, for example, Section **A, 3**), mention must, however, be made of Hillebrand and Lundell's *Applied Inorganic Analysis* (1929) and of Mitchell and Ward's *Modern Methods in Quantitative Chemical Analysis* (1932). In conclusion, the writer wishes to express his thanks: to Dr. G. H. Jeffery, A.I.C., for reading the galley proofs and making numerous helpful suggestions ; to Mr. A. S. Nickelson, B.Sc., for reading some of the galley proofs ; to his laboratory steward, Mr. F. Mathie, for preparing a number of the diagrams including most of those in Chapter VI, and for his assistance in other ways ; to Messrs. A. Gallenkamp and Co., Ltd., of London, E.C.2, and to Messrs. Fisher Scientific Co., of Pittsburgh, Pa., for providing a number of diagrams and blocks ;* and to Mr. F. W. Clifford, F.L.A., Librarian to the Chemical Society, and his able assistants for their help in the task of searching the extensive literature.

Any suggestions for improving the book will be gratefully received by the author.

Woolwich Polytechnic, London, S.E.18.
June 1939.

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* Acknowledgement to other firms and individuals is made in the body of the text.

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CHAPTER I

THE THEORETICAL BASIS OF QUANTITATIVE CHEMICAL ANALYSIS

I, 1. Electrolytic dissociation.—Many of the reactions of qualitative and quantitative analysis take place in aqueous solution. It is therefore necessary to have a general knowledge of the conditions which exist in such solutions. It is assumed that the reader is familiar with the broad concepts of Arrhenius's theory of electrolytic dissociation.*

Ionisation of acids and bases in solution.—An acid may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydrogen ions as the only positive ion :

$$HCl \rightleftharpoons H^+ + Cl^- ;$$
$$HNO_3 \rightleftharpoons H^+ + NO_3^- .$$

Actually the free hydrogen ions H^+ (or protons) do not exist in the free state in aqueous solution ; each hydrogen ion combines with one molecule of water to form the *hydroxonium ion* H_3O^+. The hydroxonium ion is a hydrated proton. The above equations are therefore more accurately written :

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- ;$$
$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^- .$$

The ionisation may be attributed to the great tendency of the free hydrogen ions H^+ or protons to combine with water molecules to form hydroxonium ions. Hydrochloric and nitric acids are almost completely dissociated in aqueous solution in accordance with the above equations ; this is readily detected by freezing point measurements and by other methods.

Polybasic acids ionise in stages. In sulphuric acid, the first hydrogen atom is almost completely ionised :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- ,$$

or

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^- .$$

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* A short account will be found in the author's *Text Book of Qualitative Chemical Analysis*, 1937 (Longmans, Green and Co.).

The second hydrogen atom is only partially ionised, except in very dilute solution :

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--},$$

or
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}.$$

Phosphoric acid also ionises in stages :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---};$$

or
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-,$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{--},$$
$$HPO_4^{--} + H_2O \rightleftharpoons H_3O^+ + PO_4^{---}.$$

The successive stages of ionisation are known as the primary, secondary and tertiary ionisations respectively. As already mentioned, these do not take place to the same degree. The primary ionisation is always greater than the secondary, and the secondary very much greater than the tertiary.

Acids of the type of acetic acid $H.C_2H_3O_2$ give an almost normal freezing point depression in aqueous solution ; the extent of dissociation is accordingly small. It is usual, therefore, to distinguish between acids which are completely or almost completely ionised in solution and those which are only slightly ionised. The former are termed **strong acids** (examples : hydrochloric, hydrobromic, hydriodic, iodic, nitric and perchloric acids, primary ionisation of sulphuric acid) and the latter are called **weak acids** (examples : nitrous acid, acetic acid, carbonic acid, boric acid, phosphorous acid, phosphoric acid, hydrocyanic acid, and hydrogen sulphide). There is, however, no sharp division between the two classes. Methods for the measurement of the relative strengths of acids are described in Section **I, 4.**

A **base** may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydroxyl ions OH^- as the only negative ions*. Thus sodium hydroxide, potassium hydroxide and the hydroxides of the alkaline earth metals are almost completely dissociated in aqueous solution :

$$NaOH \rightleftharpoons Na^+ + OH^-;$$
$$Ba(OH)_2 \rightleftharpoons Ba^{++} + 2OH^-.$$

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* A more general concept of acids and bases is due to **Brönsted** ; this is now generally accepted. He defines an **acid** as a substance which ionises to yield hydrogen ions or protons, and a **base** as a substance which combines with hydrogen ions. An acid is accordingly a proton donor and a base a protor acceptor. Both can be defined by the expression :

$$A \rightleftharpoons H^+ + B,$$

where A is the acid and B is the base.

These are **strong bases.** Ammonium hydroxide solution, however, is a **weak base.** Only a small concentration of hydroxyl ions is produced in aqueous solution :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-,$$

or

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$

Salts. The structure of numerous salts in the solid state has been investigated by means of X-rays and by other methods, and it has been shown that they are composed of charged atoms or groups of atoms held together in a crystal lattice. When these salts are dissolved in a solvent of high dielectric constant such as water, or are heated to the melting point, the crystal forces are weakened and the substances dissociate into the pre-existing charged particles or ions, so that the resultant liquids are good conductors of electricity. The complete dissociation of salts in aqueous solution is the modern view and is now almost universally accepted. There are, however, some exceptions, and these have, in some cases, been supported by X-ray measurements. Feebly ionised salts (**weak electrolytes**) are exemplified by the cyanides, thiocyanates and halides of mercury and cadmium, and by lead acetate.

The theoretical implications of the theory of complete ionisation, due to Debye, Hückel and Onsager, have been fully worked out by these authors. In particular, they have been able to account for the increasing equivalent conductance with decreasing concentration over the concentration range 0–0·002*N*. For full details the reader must be referred to text-books of physical chemistry ; a short account will be found in the author's *Text Book of Qualitative Chemical Analysis*.

It is important to realise that whilst complete ionisation occurs with strong electrolytes, this does not mean that the *effective concentrations* of the ions are the same at all concentrations, for if this were the case, the osmotic properties of aqueous solutions could not be accounted for. The variation of osmotic properties is ascribed to changes of the "*activity*" of the ions ; these are dependent upon the electrical forces between the ions. Expressions for the variations of the "activity" or of related quantities, applicable to dilute solutions, have also been deduced by the Debye-Hückel-Onsager theory. Further consideration of the conception of "activity" will be found in Section I, 5.

I, 2. THE LAW OF MASS ACTION

Guldberg and Waage in 1867 clearly stated the **law of mass action** (sometimes termed the law of chemical equilibrium) in the form: the velocity of a chemical reaction is proportional to the product of the active masses of the reacting substances. For the present we shall interpret "active mass" by concentration and express it in gram molecules (or mols) per litre. By applying the law to homogeneous systems, *i.e.*, to systems in which all the reacting molecules are present in one phase, for example in solution, we can arrive at a mathematical expression for the condition of equilibrium in a reversible reaction.

Let us consider first the simple reversible reaction at constant temperature:

$$A + B \rightleftharpoons C + D.$$

The velocity with which A and B react is proportional to their concentrations, or

$$v_1 = k_1 \times [\mathbf{A}] \times [\mathbf{B}],$$

where k_1 is a constant known as the velocity coefficient, and the square brackets in heavy type denote the molecular concentrations of the substances enclosed within the brackets. Similarly, the velocity with which the reverse reaction occurs is given by:

$$v_2 = k_2 \times [\mathbf{C}] \times [\mathbf{D}].$$

At equilibrium, the velocities of the reverse and the forward reactions will be equal (the equilibrium is a dynamic and not a static one) and therefore $v_1 = v_2$,

or $$k_1 \times [\mathbf{A}] \times [\mathbf{B}] = k_2 \times [\mathbf{C}] \times [\mathbf{D}],$$

or $$\frac{[\mathbf{C}] \times [\mathbf{D}]}{[\mathbf{A}] \times [\mathbf{B}]} = \frac{k_2}{k_1} = K.$$

K is the **equilibrium constant** of the reaction at the given temperature.

The expression may be generalised. For a reversible reaction represented by:

$$p_1A_1 + p_2A_2 + p_3A_3 + \ldots \rightleftharpoons q_1B_1 + q_2B_2 + q_3B_3 + \ldots,$$

where p_1, p_2, p_3 and q_1, q_2, q_3 are the number of molecules of reacting substances, the condition for equilibrium is given by the expression:

$$\frac{[\mathbf{B_1}]^{q_1} \times [\mathbf{B_2}]^{q_2} \times [\mathbf{B_3}]^{q_3} \ldots\ldots}{[\mathbf{A_1}]^{p_1} \times [\mathbf{A_2}]^{p_2} \times [\mathbf{A_3}]^{p_3} \ldots\ldots} = K.$$

This result may be expressed in words : When equilibrium is reached in a reversible reaction, at constant temperature, the product of the molecular concentrations of the resultants (the substances on the right hand side of the equation) divided by the product of the molecular concentrations of the reactants (the substances on the left hand side of the equation), each concentration being raised to a power equal to the number of molecules of that substance taking part in the reaction, is constant.

It must be pointed out that there is no relation between the velocity at which a reaction attains equilibrium and the equilibrium constant. The velocity of a reaction increases rapidly with rise of temperature, and is also affected by certain substances. Those substances which increase the rate of reaction are termed positive catalysts, whilst those which decrease it are called negative catalysts.

I, 3. Application of the law of mass action to solutions of electrolytes.—Weak (or slightly dissociated) electrolytes, such as acetic acid and ammonium hydroxide, undergo reversible dissociation when dissolved in water. The equilibrium between the undissociated molecules and the ions for such electrolytes can be investigated by the law of mass action. The law cannot be applied to strong electrolytes, such as salts, since dissociation is complete, or virtually complete.

The equilibrium which exists in a dilute solution of acetic acid at constant temperature is :

$$H.C_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \; \text{*}.$$

Applying the law of mass action, we have :

$$[C_2H_3O_2^-] \times [H^+] \, / \, [H.C_2H_3O_2] = K.$$

K is the **ionisation constant** or **dissociation constant** at constant temperature. The term *affinity constant* is sometimes employed for acids and bases. If one gram equivalent of the electrolyte is dissolved in V litres of solution ($V = 1/c$, where c is the concentration in gram equivalents per litre), and if a is the degree of ionisation at equilibrium, then the amount of unionised electrolyte will be $(1 - a)$ gram equivalents, and the amount of each of the ions will be a gram equivalents. The concentration (gram equivalents per litre) of unionised

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* Strictly speaking the equilibrium should be written :

$$H.C_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

no free protons (H^+) exist in aqueous solution. The older form will, however, be retained for the sake of simplicity.

acetic acid will therefore be $(1 - \alpha)/V$, and the concentration of each of the ions α/V. Substituting in the equilibrium equation, we obtain the expression :

$$\alpha^2 / (1 - \alpha)V = K \qquad \text{or } \alpha^2 c / (1 - \alpha) = K.$$

This is known as **Ostwald's dilution law.** The agreement of the " law " with experiment is illustrated by the following results for acetic acid (Table I).

TABLE I. EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C.

Concn × 10^4	Λ_e	α	$K \times 10^5$
1·873	102·5	0·264	1·78
5·160	65·95	0·170	1·76
9·400	50·60	0·130	1·83
24·78	31·94	0·080	1·82
38·86	25·78	0·066	1·83
56·74	21·48	0·055	1·84
68·71	19·58	0·050	1·84
92·16	16·99	0·044	1·84
112·2	15·41	0·040	1·84
0	388·6		

The mean classical or Ostwald dissociation constant of acetic acid at 25°C is $1{\cdot}82 \times 10^{-5}$. Similar results—the individual variations may sometimes be slightly greater—are obtained for other weak electrolytes.

I, 4. Strengths of acids and bases.—It has already been stated (Section **I, 1**) that the properties of acids are the properties of the hydrogen ion H^+ (or, more correctly, the hydroxonium ion H_3O^+). For any given total concentration of acid, the concentration of hydrogen ions will depend upon the degree of dissociation α ; the strength of an acid will thus depend upon the value of α at a given concentration. The dissociation constant gives a relationship between α and the concentration, and it accordingly also represents a measure of the strength of the acid or a measure of its tendency to undergo dissociation.

The properties of bases, according to the most elementary view, depend upon the hydroxyl ion* and the ionisation

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* See footnote, Section **I, 1**.

TABLE II. DISSOCIATION CONSTANTS AT 25°C.

Acid.	*Formula*	K_a	$pK_a = -\log K_a$
Acetic	$H.C_2H_3O_2$	$1{\cdot}82 \times 10^{-5}$	4·75
		$1{\cdot}76 \times 10^{-5}$ †	4·75
Benzoic	$H.C_7H_5O_2$	$6{\cdot}37 \times 10^{-5}$ †	4·20
o-Chlorobenzoic	$H.C_7H_4O_2Cl$	$1{\cdot}20 \times 10^{-3}$ †	2·92
Formic	$H.CHO_2$	$1{\cdot}77 \times 10^{-4}$ †	3·75
Furoic	$H.C_5H_3O_3$	$6{\cdot}78 \times 10^{-5}$ †	4·17
Hydrocyanic	$H.CN$	$7{\cdot}2 \times 10^{-10}$	9·14
Nitrous	$H.NO_2$	$4{\cdot}6 \times 10^{-4}$	3·33
o-Nitrobenzoic	$H.C_7H_4O_2.NO_2$	$6{\cdot}00 \times 10^{-4}$ †	3·22
Phenylacetic	$H.C_8H_7O_2$	$4{\cdot}88 \times 10^{-5}$ †	4·31
Adipic	$H_2.C_6H_8O_4$	K_1 $3{\cdot}72 \times 10^{-5}$ †	4·43
		K_2 $3{\cdot}86 \times 10^{-6}$ †	5·41
Carbonic	$H_2.CO_3$	K_1 $4{\cdot}31 \times 10^{-7}$ †	6·37
		K_2 $5{\cdot}61 \times 10^{-11}$ †	10·25
Hydrogen Sulphide	$H_2.S$	K_1 $9{\cdot}1 \times 10^{-8}$	7·04
		K_2 $1{\cdot}2 \times 10^{-15}$	14·92
Malonic	$H_2.C_3H_2O_4$	K_1 $1{\cdot}40 \times 10^{-3}$ †	2·85
		K_2 $2{\cdot}20 \times 10^{-6}$ †	5·66
Oxalic	$H_2.C_2O_4$	K_1 $5{\cdot}9 \times 10^{-2}$ †	1·23
		K_2 $6{\cdot}4 \times 10^{-5}$ †	4·19
Phthalic	$H_2.C_8H_4O_4$	K_1 $1{\cdot}2 \times 10^{-3}$	2·92
		K_2 1×10^{-5}	5·00
Succinic	$H_2.C_4H_4O_4$	K_1 $6{\cdot}63 \times 10^{-5}$ †	4·18
		K_2 $2{\cdot}54 \times 10^{-6}$ †	5·60
Sulphuric	$H_2.SO_4$	K_2 $1{\cdot}15 \times 10^{-2}$ †	1·94
Sulphurous	$H_2.SO_3$	K_1 $1{\cdot}7 \times 10^{-2}$	1·77
		K_2 $1{\cdot}0 \times 10^{-7}$	7·00
d-Tartaric	$H_2.C_4H_4O_6$	K_1 $1{\cdot}04 \times 10^{-3}$ †	2·98
		K_2 $4{\cdot}55 \times 10^{-5}$ †	4·34
Boric	$H.H_2BO_3$	K_1 $5{\cdot}80 \times 10^{-10}$ †	9·24
Citric	$H_3.C_6H_5O_7$	K_1 $9{\cdot}20 \times 10^{-4}$ †	3·04
		K_2 $2{\cdot}69 \times 10^{-5}$ †	4·57
		K_3 $1{\cdot}34 \times 10^{-6}$ †	5·87
Phosphoric	$H_3.PO_4$	K_1 $7{\cdot}52 \times 10^{-3}$ †	2·12
		K_2 $6{\cdot}23 \times 10^{-8}$ †	7·21
		K_3 5×10^{-13} †	12·30
Base		K_b	$pK_b = -\log K$
Ammonium hydroxide	NH_4OH	$1{\cdot}8 \times 10^{-5}$	4·74
		$1{\cdot}79 \times 10^{-5}$ †	4·75
Aniline	$C_6H_5NH_2$ *	$4{\cdot}0 \times 10^{-10}$	9·40
Ethylamine	$C_2H_5NH_2$ *	$4{\cdot}6 \times 10^{-4}$	3·34
Dimethylamine	$(CH_3)_2NH$ *	$5{\cdot}20 \times 10^{-4}$ †	3·28
Methylamine	CH_3NH_2 *	$4{\cdot}38 \times 10^{-4}$ †	3·36
Piperidine	$C_5H_{11}N$ *	$1{\cdot}3 \times 10^{-3}$	2·88
Quinoline	C_9H_7N *	$6{\cdot}0 \times 10^{-10}$	9·22
Trimethylamine	$(CH_3)_3N$ *	$5{\cdot}45 \times 10^{-4}$ †	3·26
Calcium hydroxide	$Ca(OH)_2$	K_2 $3{\cdot}1 \times 10^{-2}$ †	1·51
Barium hydroxide	$Ba(OH)_2$	K_2 $2{\cdot}3 \times 10^{-1}$ †	0·64

* All compounds marked with an asterisk are of the ammonium type, *e.g.*, aniline is really anilinium hydroxide :

$$(C_6N_5NH_3)OH \rightleftharpoons (C_6H_5NH_3)^+ + OH^-.$$

† Figures marked with a † are the true or thermodynamic dissociation constants. (See Section I, 5.)

constant will likewise be a measure of the strength of the base.

For very weak or slightly ionised electrolytes, the expression $\alpha^2/(1 - \alpha)V = K$ reduces to $\alpha^2 = KV$ or $\alpha = \sqrt{KV}$, since α may be neglected in comparison with unity. Hence for any two weak acids or bases at a given dilution V (in litres), we have $\alpha_1 = \sqrt{K_1V}$ and $\alpha_2 = \sqrt{K_2V}$, or $\alpha_1/\alpha_2 = \sqrt{K_1}/\sqrt{K_2}$. Expressed in words, for any two weak or slightly dissociated electrolytes at equal dilutions, the degrees of dissociation are proportional to the square roots of their ionisation constants. Some values for the dissociation constants at 25°C for weak acids and bases are collected in Table II.

I, 5. Activity and activity coefficient.—In our deduction of the law of mass action it was assumed that the effective concentrations or active masses of the components could be expressed by the stoichiometric concentrations. According to modern thermodynamics, this is not strictly true. The rigid equilibrium equation for, say, a binary electrolyte :

$$AB \rightleftharpoons A^+ + B^-,$$

is

$$a_{A^+} \times a_{B^-} / a_{AB} = K_a,$$

where a_{A^+}, a_{B^-} and a_{AB} represent the **activities** of A^+, B^- and AB respectively, and K_a is the **true** or **thermodynamic dissociation constant.** The concept of **activity,** a thermodynamic quantity, is due to G. N. Lewis. The quantity is related to the concentration by a factor, termed the **activity coefficient** :

activity = concentration × activity coefficient.

Thus at any molar concentration

$$a_{A^+} = f_{A^+}.[A^+],\ a_{B^-} = f_{B^-}.[B^-], \text{ and } a_{AB} = f_{AB}\cdot[AB],$$

where f refers to the activity coefficients, and the square brackets to the molar concentrations. Substituting in the above equation, we obtain :

$$\frac{f_{A^+}.[A^+] \times f_{B^-}.[B^-]}{f_{AB}\cdot[AB]} = \frac{[A^+].[B^-]}{[AB]} \times \frac{f_{A^+} \times f_{B^-}}{f_{AB}} = K_a.$$

This is the rigorously correct expression for the law of mass action as applied to weak electrolytes.

The activity coefficient varies with the concentration. For ions, it varies with the valency, and is the same for all *dilute* solutions having the same **ionic strength,** the latter being a measure of the electrical field existing in the solution. The term ionic strength, designated by the symbol μ, was introduced by Lewis and Randall in 1921, and is defined as equal to one half of the sum of the products of the concentration of each ion multiplied by the square of its valency, or $\mu = 0{\cdot}5\Sigma c_i z_i^2$, where c_i is the ionic concentration in gram mols per litre of solution and z_i is the valency of the ion concerned. An example will make this clear. The ionic strength of 0·1 molar HNO_3 solution containing 0·2 molar $Ba(NO_3)_2$ is given by:

$$0{\cdot}5\{0{\cdot}1 \text{ (for H}^+) + 0{\cdot}1 \text{ (for NO}_3^-) + 0{\cdot}2 \times 2^2 \text{ (for Ba}^{++}) + 0{\cdot}2 \times 2 \text{ (for NO}_3^-)\}$$
$$= 0{\cdot}5\ \{1{\cdot}4\} = 0{\cdot}7.$$

The activity coefficient depends upon the *total* ionic strength of the solution in a manner which is discussed in Section **I, 10.** Generally speaking, it is comparatively difficult to determine activity coefficients experimentally, particularly in concentrated solutions and in mixtures of ions of several valency types. The activity coefficients of unionised molecules do not differ considerably from unity. For weak electrolytes in which the ionic concentration and therefore the ionic strength is small, the error introduced by neglecting the difference between the actual values of the activity coefficients of the ions, f_{A^+} and f_{B^-}, and unity is small ($<$ 5 per cent.). Hence for weak electrolytes, the true or thermodynamic expression reduces to $[A^+] \times [B^-] / [AB] = K$; the constants obtained by the use of simple concentrations will be accurate to 2–6 per cent. Such values are sufficiently precise for purposes of calculation in quantitative analysis. It must, however, be pointed out that precision values for the dissociation constants of weak electrolytes can be obtained by the use of special methods; the discussion of these is outside the scope of this volume.

Strong electrolytes will be assumed to be completely dissociated, and no correction for activity coefficients will be made for dilute solutions.

I, 6. Ionisation of polybasic acids.—When a polybasic acid is dissolved in water, the various hydrogen atoms undergo ionisation to different extents. For a **dibasic acid** H_2A, the primary and secondary ionisations can be represented by the equations:

$$H_2A \rightleftharpoons H^+ + HA^- \qquad (1);$$
$$HA^- \rightleftharpoons H^+ + A^{--} \qquad (2).$$

If the dibasic acid is a weak electrolyte, the law of mass action may be applied, and the following expressions obtained :

$$[H^+] \times [HA^-] / [H_2A] = K_1 \qquad (1A),$$

$$[H^+] \times [A^{--}] / [HA^-] = K_2 \qquad (2A).$$

K_1 and K_2 are known as the **primary** and **secondary dissociation constants** respectively. Each stage of the dissociation process has its own ionisation constant, and the magnitudes of these constants give a measure of the extent to which each ionisation has proceeded at any given concentration. The greater the value of K_1 relative to K_2, the smaller will be the secondary dissociation, and the greater must be the dilution before the latter becomes appreciable. It is therefore possible that a dibasic (or polybasic) acid may behave, so far as dissociation is concerned, as a monobasic acid. This is indeed characteristic of many polybasic acids (see Table II).

A **tribasic acid** H_3A (*e.g.*, orthophosphoric acid) will similarly yield three dissociation constants, K_1, K_2 and K_3, which may be computed in an analogous manner :

$$H_3A \rightleftharpoons H^+ + H_2A^- \qquad (3) ;$$

$$H_2A^- \rightleftharpoons H^+ + HA^{--} \qquad (4) ;$$

$$HA^{--} \rightleftharpoons H^+ + A^{---} \qquad (5).$$

We can now apply some of the theoretical considerations to actual examples encountered in analysis.

Example 1. To calculate the concentrations of HS^- and S^{--} in a saturated solution of hydrogen sulphide.

A saturated aqueous solution of hydrogen sulphide at 25°C, at atmospheric pressure, is approximately 0·1 molar. The primary and secondary dissociation constants are $9{\cdot}1 \times 10^{-8}$ and $1{\cdot}2 \times 10^{-15}$ respectively.

Thus $\quad [H^+] \times [HS^-] / [H_2S] = 9{\cdot}1 \times 10^{-8} \qquad$ (i),

and $\quad [H^+] \times [S^{--}] / [HS^-] = 1{\cdot}2 \times 10^{-15} \qquad$ (ii).

The very much smaller value of K_2 indicates that the secondary dissociation and consequently $[S^{--}]$, is exceedingly small. It follows, therefore, that only the primary ionisation is of importance, and $[H^+]$ and $[HS^-]$ are practically equal in value. Substituting in equation (i) :

$[H^+] = [HS^-]$ and $[H_2S] = 0{\cdot}1$, we obtain

$$[H^+] = [HS^-] = \sqrt{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1} = 9{\cdot}5 \times 10^{-5}.$$

Both the equilibrium equations must be satisfied simultaneously ; by substitution of these values for $[H^+]$ and $[HS^-]$ in equation (ii), we obtain $9{\cdot}5 \times 10^{-5} \times [S^{--}] = 1{\cdot}2 \times 10^{-15} \times 9{\cdot}5 \times 10^{-5}$, or $[S^{--}] = 1{\cdot}2 \times 10^{-15}$, which is the value for K_2.

If we multiply equations (i) and (ii) together and transpose :

$$[S^{--}] = 1{\cdot}1 \times 10^{-23} / [H^+]^2.$$

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen ion concentration, *i.e.*, if we, say, double $[H^+]$ by the addition of a strong acid, the $[S^{--}]$ would be reduced to $1/2^2$ or $1/4$ of its original value.

I, 7. Common ion effect.—The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound which produces that ion upon dissociation. The particular ion is thus derived from the compound already in solution and from the added reagent, hence the name **common ion.** We shall confine our attention to the case in which the original compound is a weak electrolyte in order that the law of mass action may be applicable. The result is usually that there is a higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced. Examples of the calculation of the common ion effect are given below. In general, it may be stated that if the total concentration of the common ion is only slightly greater than that which the original compound alone would furnish, the effect is small ; if, however, the concentration of the common ion is very much increased (*e.g.*, by the addition of a completely dissociated salt), the effect is very great and may be of considerable practical importance. Indeed, the common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

Example 2. To calculate the sulphide ion concentration in a 0·25 molar hydrochloric acid solution saturated with hydrogen sulphide.

This concentration has been chosen since it is that at which the sulphides of the metals of Group II are precipitated. The total concentration of hydrogen sulphide will be approximately the same as in aqueous solution, *i.e.*, $0{\cdot}1M$; the $[H^+]$ will be equal to that of the completely dissociated HCl, *i.e.*, $0{\cdot}25M$, but the $[S^{--}]$ will be reduced below $1{\cdot}2 \times 10^{-15}$

Substituting in equations (i) and (ii) (Section **I, 6**), we find :

$$[HS^-] = \frac{9{\cdot}1 \times 10^{-8} \times [H_2S]}{[H^+]} = \frac{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1}{0{\cdot}25} = 3{\cdot}6 \times 10^{-8},$$

$$[S^{--}] = \frac{1{\cdot}2 \times 10^{-15} \times [HS^-]}{[H^+]} = \frac{1{\cdot}2 \times 10^{-15} \times 3{\cdot}6 \times 10^{-8}}{0{\cdot}25}$$

$$= \mathit{1{\cdot}7} \times \mathit{10^{-22}}.$$

Thus by changing the acidity from $9{\cdot}5 \times 10^{-5}M$ (that present in saturated H_2S water) to $0{\cdot}25M$, the sulphide ion concentration is reduced from $1{\cdot}2 \times 10^{-15}$ to $1{\cdot}7 \times 10^{-22}$.

Example 3. What effect has the addition of 0·1 gram molecule (8·20 g.) of anhydrous sodium acetate to 1 litre of 0·1 molar acetic acid upon the degree of dissociation of the acid ?

The dissociation constant of acetic acid at 25°C is $1{\cdot}82 \times 10^{-5}$. The degree of ionisation α in $0{\cdot}1M$ solution ($c = 0{\cdot}1$) may be computed by solving the quadratic equation :

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{\alpha^2 c}{(1-\alpha)} = 1{\cdot}82 \times 10^{-5}.$$

For our purpose it is sufficiently accurate to neglect α in $(1 - \alpha)$ since α is small :

$$\therefore\ \alpha = \sqrt{Kc} = \sqrt{1{\cdot}82 \times 10^{-4}} = 0{\cdot}0135.$$

Hence in $0{\cdot}1M$ acetic acid,

$[H^+] = 0{\cdot}00135$, $[C_2H_3O_2^-] = 0{\cdot}00135$, and $[H.C_2H_3O_2] = 0{\cdot}0986$. The concentrations of sodium and acetate ions produced by the addition of the completely dissociated sodium acetate are :

$[Na^+] = 0{\cdot}1$, and $[C_2H_3O_2^-] = 0{\cdot}1$ gram molecule respectively. The acetate ions from the salt will tend to decrease the ionisation of the acetic acid since K is constant, and consequently the acetate ion concentration derived from it. Hence we may write $[C_2H_3O_2^-] = 0{\cdot}1$ for the solution, and if α' is the new degree of ionisation, $[H^+] = \alpha' c = 0{\cdot}1\alpha'$, and $[H.C_2H_3O_2] = (1 - \alpha')c = 0{\cdot}1$, since α' is negligibly small.

Substituting in the mass action equation :

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{0{\cdot}1\alpha' \times 0{\cdot}1}{0{\cdot}1} = 1{\cdot}82 \times 10^{-5},$$

$$or \quad \alpha' = 1{\cdot}8 \times 10^{-4}.$$

$$[H^+] = \alpha' c = \mathit{1{\cdot}8} \times \mathit{10^{-5}}.$$

The addition of a tenth of an equivalent weight of sodium acetate to a 0·1 molar solution of acetic acid has decreased the degree of ionisation from 1·35% to 0·018%, and the hydrogen ion concentration from 0·0135 to 0·000018.

Example 4. What effect has the addition of 0·5 gram molecule (26·75 g.) of ammonium chloride to 1 litre of 0·1 molar ammonium hydroxide solution upon the degree of dissociation of the base ?

(Dissociation constant of $NH_4OH = 1{\cdot}8 \times 10^{-5}$.)

In $0{\cdot}1M$ ammonia solution $\alpha = \sqrt{1{\cdot}8 \times 10^{-5} \times 0{\cdot}1} = 0{\cdot}013$. Hence $[OH^-] = 0{\cdot}0013$, $[NH_4^+] = 0{\cdot}0013$, and $[NH_4OH] = 0{\cdot}0987$. Let α' be the degree of ionisation in the presence of the added ammonium chloride. Then $[OH^-] = \alpha'c = 0{\cdot}1\alpha'$, and $[NH_4OH] = (1 - \alpha')c = 0{\cdot}1$, since α' may be taken as negligibly small. The addition of the completely ionised ammonium chloride will of necessity decrease the $[NH_4{}^+]$ derived from the base and increase $[NH_4OH]$, since K is constant under all conditions. Now $[NH_4{}^+] = 0{\cdot}5$, as a first approximation.

Substituting in the equation :

$$\frac{[NH_4{}^+] \times [OH^-]}{[NH_4OH]} = \frac{0{\cdot}5 \times 0{\cdot}1\alpha'}{0{\cdot}1} = 1{\cdot}8 \times 10^{-5},$$

$$\text{or} \qquad \alpha' = 3{\cdot}6 \times 10^{-5} \text{ and } [OH^-] = 3{\cdot}6 \times 10^{-6}.$$

The addition of half an equivalent weight of ammonium chloride to a 0·1 molar solution of ammonium hydroxide has decreased the degree of ionisation from 1·35% to 0·0036%, and the hydroxyl ion concentration from 0·0013 to 0·0000036.

I, 8. Solubility product.—For sparingly soluble salts (*i.e.*, those of which the solubility is less than 0·01 gram molecules per litre) it is an experimental fact that the product of the total molecular concentrations of the ions is a constant at constant temperature. This product S is termed the **solubility product.** For a binary electrolyte :

$$AB \rightleftharpoons A^+ + B^-,$$
$$S_{AB} = [A^+] \times [B^-].$$

In general, for an electrolyte A_pB_q, which ionises into $pA^{+\cdots}$ and $qB^{-\cdots}$ ions :

$$A_pB_q \rightleftharpoons pA^{+\cdots} + qB^{-\cdots},$$
$$S_{A_pB_q} = [A^{+\cdots}]^p \times [B^{-\cdots}]^q.$$

A plausible deduction of the solubility product relation is the following. When excess of a sparingly soluble electrolyte, say silver chloride, is shaken up with water, some of it passes into solution to form a saturated solution of the salt and the reaction appears to cease. The following equilibrium is actually present (the silver chloride is completely ionised in solution) :

$$AgCl\ (\text{solid}) \rightleftharpoons Ag^+ + Cl^-.$$

The velocity of the forward reaction depends only upon the temperature, and at any given temperature :

$$v_1 = k_1,$$

where k_1 is a constant. The velocity of the reverse reaction is proportional to the concentrations of each of the reacting substances ; hence at any given temperature :

$$v_2 = k_2 \times [Ag^+] \times [Cl^-],$$

where K_2 is another constant. At equilibrium the two velocities are equal,

$$i.e., \; k_1 = k_2 \times [Ag^+] \times [Cl^-],$$

or

$$[Ag^+] \times [Cl^-] = k_1/k_2 = S_{AgCl} .$$

A more rigid deduction of the solubility product principle can be obtained along the following lines. For simplicity, we shall again consider a binary electrolyte :

$$AB \rightleftharpoons A^+ + B^-.$$

The solid is completely dissociated in dilute solution ; no undissociated molecules will therefore be present. It can be shown by thermodynamics that in a saturated solution of any salt containing varying amounts of a more soluble salt with a common ion, the products of the activities of the two ions in the various saturated solutions are the same :

$$i.e., \; a_{A^+} \times a_{B^-} = \text{constant } (\textbf{activity product}).$$

In the very dilute solutions with which we are at present concerned, the activities may be taken as practically equal to the concentrations,* so that $[A^+] \times [B^-] = \text{constant}$.

Some experimental results, due to Jahn (1904), illustrating the approximate constancy of the solubility product of silver chloride in the presence of varying concentrations of chloride ion (from potassium chloride) are collected in Table III.

TABLE III. EFFECT OF CHLORIDE IONS UPON THE SOLUBILITY PRODUCT OF AgCl.

[KCl]	$[Cl^-] \times 10^3$	$[Ag^+] \times 10^8$	$S_{AgCl} = [Ag^+].[Cl^-] \times 10^{10}$
0·00670	6·4	1·75	1·12
0·00833	7·9	1·39	1·10
0·01114	10·5	1·07	1·12
0·01669	15·5	0·74	1·14
0·03349	30·3	0·39	1·14

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* Activity = activity coefficient × concentration, i.e., $a = fc$. The activity product may therefore be written :

$$f_{A^+}[A^+] \times f_{B^-}[B^-] = \text{constant}.$$

In very dilute solution f is proportional to $(1 - k\sqrt{c})$, and if c is small, this quantity is approximately unity.

It is important to note that the solubility product relation applies with sufficient accuracy for purposes of quantitative analysis only to saturated solutions of slightly soluble electrolytes and with *small* additions of other salts. In the presence of large concentrations of salts, the ionic concentration, and therefore the ionic strength of the solution, will increase. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant (see Section **I, 10** for a more detailed discussion).

The great importance of the conception of solubility product lies in its bearing upon precipitation from solution, which is, of course, one of the principal operations of quantitative analysis. The solubility product is the ultimate value which is attained by the ionic product when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution. If the experimental conditions are such that the ionic product is different from the solubility product, then the system will attempt to adjust itself in such a manner that the ionic and solubility products are equal in value. Thus, if, for a given electrolyte, the product of the concentrations of the ions in solution is arbitrarily made to exceed the solubility product, as, for example, by the addition of a salt with a common ion, the adjustment of the system to equilibrium results in the precipitation of the solid salt, provided supersaturation conditions are excluded. If the ionic product is less than the solubility product or can arbitrarily be made so, as, for example, by complex salt formation or by the formation of weak electrolytes, then a further quantity of solute can pass into solution until the solubility product is attained, or, if this is not possible, until all the solute has dissolved.

Table IV contains the solubility products (S) at the laboratory temperature (*ca.* 20°C) of some common sparingly soluble substances. Values for $pS = -\log_{10} S$ are given in the last column. The student is referred to text-books of physical chemistry for a description of the methods for determining solubility products. It must, however, be pointed out that the various methods do not always yield consistent results, and what appear to be the best representative figures are given in the Table.

TABLE IV. SOLUBILITY PRODUCTS AT THE LABORATORY TEMPERATURE.

Substance	*Solubility Product*	*pS*	*Substance*	*Solubility Product*	*pS*
AgBr	$3{\cdot}5 \times 10^{-13}$	12·46	FeS	$1{\cdot}5 \times 10^{-19}$	18·82
AgCNS	$7{\cdot}1 \times 10^{-13}$	12·15	Hg_2Br_2	$1{\cdot}3 \times 10^{-18}$	17·89
AgCl	$1{\cdot}2 \times 10^{-10}$	9·92	Hg_2Cl_2	$2{\cdot}0 \times 10^{-21}$	20·70
Ag_2CrO_4	$1{\cdot}7 \times 10^{-12}$	11·77	Hg_2I_2	$1{\cdot}2 \times 10^{-28}$	27·92
AgI	$1{\cdot}7 \times 10^{-16}$	15·77	HgS	4×10^{-53}	52·4
Ag_3PO_4	$1{\cdot}8 \times 10^{-18}$	17·74	$KH.C_4H_4O_6$	$3{\cdot}0 \times 10^{-4}$	3·52
Ag_2S	$1{\cdot}6 \times 10^{-49}$	48·80	K_2PtCl_6	$4{\cdot}9 \times 10^{-5}$	4·31
$Al(OH)_3$	$8{\cdot}5 \times 10^{-23}$	22·07	$MgCO_3$	$2{\cdot}6 \times 10^{-5}$	4·58
$BaCO_3$	$1{\cdot}9 \times 10^{-9}$	8·72	MgC_2O_4	$8{\cdot}6 \times 10^{-5}$	4·07
BaC_2O_4	$1{\cdot}7 \times 10^{-7}$	6·77	MgF_2	$7{\cdot}0 \times 10^{-9}$	8·15
$BaCrO_4$	$2{\cdot}3 \times 10^{-10}$	9·64	$Mg(NH_4)PO_4$	$2{\cdot}5 \times 10^{-13}$	12·60
$BaSO_4$	$1{\cdot}2 \times 10^{-10}$	9·92	$Mg(OH)_2$	$1{\cdot}5 \times 10^{-11}$	10·82
$CaCO_3$	$1{\cdot}7 \times 10^{-8}$	7·77	$Mn(OH)_2$	$4{\cdot}0 \times 10^{-14}$	13·40
CaC_2O_4	$3{\cdot}8 \times 10^{-9}$	8·42	MnS	$1{\cdot}4 \times 10^{-15}$	14·85
$Ca.C_4H_4O_6$ (tartrate)	$7{\cdot}7 \times 10^{-7}$	6·11	$Ni(OH)_2$	$8{\cdot}7 \times 10^{-19}$	18·06
			NiS	$1{\cdot}4 \times 10^{-24}$	23·85
CaF_2	$3{\cdot}2 \times 10^{-11}$	10·49	$PbBr_2$	$7{\cdot}9 \times 10^{-5}$	4·10
$CaSO_4$	$2{\cdot}3 \times 10^{-4}$	3·64	$PbCl_2$	$2{\cdot}4 \times 10^{-4}$	3·62
CdS	$3{\cdot}6 \times 10^{-29}$	28·44	$PbCO_3$	$1{\cdot}7 \times 10^{-11}$	10·77
$Co(OH)_2$	$1{\cdot}6 \times 10^{-18}$	17·80	$PbCrO_4$	$1{\cdot}8 \times 10^{-14}$	13·74
CoS	$1{\cdot}9 \times 10^{-27}$	26·72	PbF_2	$7{\cdot}0 \times 10^{-9}$	8·15
$Cr(OH)_3$	$2{\cdot}9 \times 10^{-29}$	28·54	PbI_2	$1{\cdot}4 \times 10^{-8}$	7·85
$Cu_2(CNS)_2$	$1{\cdot}7 \times 10^{-11}$	10·77	PbS	$4{\cdot}2 \times 10^{-28}$	27·38
Cu_2Br_2	$4{\cdot}1 \times 10^{-8}$	7·39	$PbSO_4$	$2{\cdot}3 \times 10^{-8}$	7·64
Cu_2Cl_2	$1{\cdot}4 \times 10^{-6}$	5·85	$SrCO_3$	$4{\cdot}6 \times 10^{-9}$	8·34
Cu_2I_2	$2{\cdot}6 \times 10^{-12}$	11·58	SrC_2O_4	$1{\cdot}4 \times 10^{-7}$	6·85
CuS	$8{\cdot}5 \times 10^{-45}$	44·07	$SrSO_4$	$3{\cdot}6 \times 10^{-7}$	6·44
$Fe(OH)_2$	$1{\cdot}6 \times 10^{-14}$	13·80	$Zn(OH)_2$	$1{\cdot}0 \times 10^{-18}$	18·00
$Fe(OH)_3$	$1{\cdot}1 \times 10^{-36}$	35·96	ZnS	*ca.* 1×10^{-20}	20·0

A few examples may help the reader to fully understand the subject. The concentrations are expressed in gram mols per litre for the calculation of solubility products.

Example 5. The solubility of silver chloride is 0·0015 grams per litre. Calculate the solubility product.

The molecular weight of silver chloride is 143·5. The solubility is therefore $0{\cdot}0015/143{\cdot}5 = 1{\cdot}05 \times 10^{-5}$ mols per litre. In a saturated solution the dissociation, $AgCl \rightleftharpoons Ag^+ + Cl^-$, is complete; 1 mol of AgCl will give 1 mol each of Ag^+ and Cl^-. Hence $[Ag^+] = 1{\cdot}05 \times 10^{-5}$ and $[Cl^-] = 1{\cdot}05 \times 10^{-5}$.

$$S_{AgCl} = [Ag^+] \times [Cl^-] = (1{\cdot}05 \times 10^{-5}) \times (1{\cdot}05 \times 10^{-5})$$
$$= \mathit{1{\cdot}1 \times 10^{-10}}.$$

Example 6. Calculate the solubility product of silver chromate, given that its solubility is $2{\cdot}5 \times 10^{-2}$ grams per litre.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{--}.$$

The molecular weight of Ag_2CrO_4 is 332, hence the solubility $= 2{\cdot}5 \times 10^{-2}/332 = 7{\cdot}5 \times 10^{-5}$ mols per litre.

Now 1 mol of Ag_2CrO_4 gives two mols of Ag^+ and 1 mol of CrO_4^{--}, therefore $S_{Ag_2CrO_4} = [Ag^+]^2 \times [CrO_4^{--}]$

$$= (2 \times 7{\cdot}5 \times 10^{-5})^2 \times (7{\cdot}5 \times 10^{-5})$$
$$= \mathit{1{\cdot}7} \times \mathit{10^{-12}}.$$

Example 7. The solubility product of magnesium hydroxide is $3{\cdot}4 \times 10^{-11}$. Calculate its solubility in grams per litre.

$$Mg(OH)_2 \text{ (solid)} \rightleftharpoons Mg^{++} + 2OH^-.$$
$$[Mg^{++}] \times [OH^-]^2 = 3{\cdot}4 \times 10^{-11}.$$

The molecular weight of magnesium hydroxide is 58. Each mol of magnesium hydroxide, when dissolved, yields one mol of magnesium ions and two mols of hydroxyl ions. If the solubility is x gram mols per litre, $[Mg^{++}] = x$ and $[OH^-] = 2x$. Substituting these values in the solubility product expression :

$$x \times (2x)^2 = 3{\cdot}4 \times 10^{-11}$$
$$\text{or} \quad x = 2{\cdot}0 \times 10^{-4} \text{ g. mols per litre}$$
$$= 2{\cdot}0 \times 10^{-4} \times 58 = \mathit{1{\cdot}2} \times \mathit{10^{-2}}\ \mathit{g.\ per\ litre.}$$

I, 9. Completeness of precipitation. Quantitative effects of a common ion.—An important application of the solubility product principle is to the calculation of the solubility of sparingly soluble salts in solution of salts with a common ion. Thus the solubility of a salt MA in the presence of a relatively large amount of the common M^+ ions,* supplied by a second salt MB, follows from the definition of solubility product :

$$[M^+] \times [A^-] = S_{MA}$$
$$\text{or} \quad [A^-] = S_{MA} / [M^+] \qquad \text{(i).}$$

The solubility of the salt is represented by the $[A^-]$ which it furnishes in solution. It is clear that the addition of a common ion will *decrease* the solubility of the salt.

Example 8. Calculate the solubility of silver chloride in $0{\cdot}001M$ and $0{\cdot}01M$ sodium chloride solutions respectively ($S_{AgCl} = 1{\cdot}1 \times 10^{-10}$).

In a saturated solution of silver chloride
$[Cl^-] = \sqrt{1{\cdot}1 \times 10^{-10}} = 1{\cdot}05 \times 10^{-5}$ g. mol per litre ; this may be neglected in comparison with the excess of Cl^- ions added.

---

* This enables us to neglect the concentration of M^+ ions supplied by the sparingly soluble salt itself, and thus to simplify the calculation.

$$\text{For } [\text{Cl}^-] = 1 \times 10^{-3}, [\text{Ag}^+] = 1{\cdot}1 \times 10^{-10}/1 \times 10^{-3}$$
$$= 1{\cdot}1 \times 10^{-7} \text{ g. mol per litre.}$$
$$\text{For } [\text{Cl}^-] = 1 \times 10^{-2}, [\text{Ag}^+] = 1{\cdot}1 \times 10^{-10}/1 \times 10^{-2}$$
$$= 1{\cdot}1 \times 10^{-8} \text{ g. mol per litre.}$$

Thus the solubility is decreased 100 times in 0·001*M* sodium chloride and 1000 times in 0·01*M* sodium chloride. Similar results are obtained for 0·001*M* and 0·01*M* silver nitrate solution.

Example 9. Calculate the solubilities of silver chromate in 0·001*M* and 0·01*M* silver nitrate solutions, and in 0·001*M* and 0·01*M* potassium chromate solutions (Ag_2CrO_4 : S.P. $= 1{\cdot}7 \times 10^{-12}$, solubility $= 7{\cdot}5 \times 10^{-5}$ mols per litre).

$$[\text{Ag}^+]^2 \times [\text{CrO}_4^{--}] = 1{\cdot}7 \times 10^{-12},$$
or
$$[\text{CrO}_4^{--}] = 1{\cdot}7 \times 10^{-12} / [\text{Ag}^+]^2.$$

For 0·001*M* silver nitrate solution : $[\text{Ag}^+] = 1 \times 10^{-3}$,

$\therefore [\text{CrO}_4^{--}] = 1{\cdot}7 \times 10^{-12}/1 \times 10^{-6} = 1{\cdot}7 \times 10^{-6}$ *mols per litre.*

For 0·01*M* silver nitrate solution :

$[\text{CrO}_4^{--}] = 1{\cdot}7 \times 10^{-12} / 1 \times 10^{-4} = 1{\cdot}7 \times 10^{-8}$ *mols per litre*

The solubility product equation gives :

$$[\text{Ag}^+] = \sqrt{1{\cdot}7 \times 10^{-12} / [\text{CrO}_4^{--}]}.$$

$$\text{For } [\text{CrO}_4^{--}] = 0{\cdot}001, [\text{Ag}^+] = \sqrt{1{\cdot}7 \times 10^{-12} / 1 \times 10^{-3}}$$
$$= 4{\cdot}1 \times 10^{-5} \text{ mols per litre.}$$
$$\text{For } [\text{CrO}_4^{--}] = 0{\cdot}01, [\text{Ag}^+] = \sqrt{1{\cdot}7 \times 10^{-12} / 1 \times 10^{-2}}$$
$$= 1{\cdot}3 \times 10^{-5} \text{ mols per litre.}$$

This decrease in solubility by the common ion effect is of fundamental importance in gravimetric analysis. By the addition of a suitable excess of a precipitating agent, the solubility of a precipitate is usually decreased to so small a value that the loss by washing is negligible. Let us consider a specific case—the determination of silver as silver chloride. Here the chloride solution is added to the solution of the silver salt. If an exactly equivalent amount is added, the resultant saturated solution of silver chloride will contain 0·0015 g. per litre (*Example* 5). If 0·2 g. of silver chloride is produced and the volume of the solution and washings is 500 ml, the loss, owing to solubility, will be 0·00075 g. or 0·33 per cent. of the weight of the salt ; the analysis would then be 0·33 per cent. too low. By using an excess of the precipitant, say, to a concentration of 0·01*M*, the solubility of the silver chloride is reduced to $1{\cdot}5 \times 10^{-5}$ g. per litre (*Example* 8), and the loss will be $1{\cdot}5 \times 10^{-5} \times 0{\cdot}5 \times 100/0{\cdot}2 = 0{\cdot}0033$ per cent. Silver chloride is therefore very suitable for the quantitative determination of silver with high accuracy.

I, 10. Limitations of the solubility product principle.—For a binary electrolyte MA, thermodynamical considerations lead to the result that the product of the activities of the two ions is constant at constant temperature :

i.e., $a_{M^+} \times a_{A^-}$ = constant (activity product $= fS_{MA}$) (1). Now activity = concentration × activity coefficient, or $a = cf$. Substituting in (1), we obtain :

$$[M^+]f_{M^+} \times [A^-]f_{A^-} = fs_{MA} \qquad (2).$$

in which f_{M^+} and f_{A^-} denote the activity coefficients of M^+ and A^- respectively. For a saturated solution of a sparingly soluble salt in water, the ionic concentration is so small that f_{M^+} and f_{A^-} are not far removed from unity and the expression (1) reduces to the classical solubility product equation.

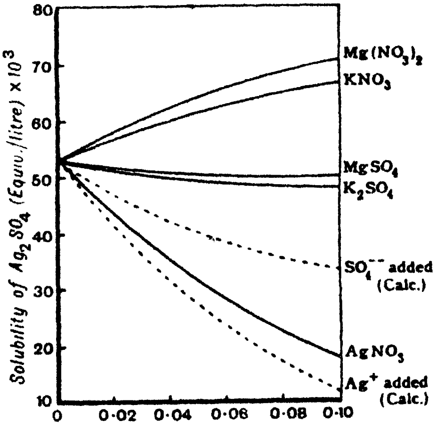

FIG. 1-2.—Influence of various salts on the solubility of Ag_2SO_4.

Numerous experiments have been carried out to determine the accuracy with which the solubility product principle applies. Some results of Bray and Winninghoff (1911) upon the solubility of thallous chloride in the presence of various salts are shown in Fig. 1-1. The dotted line represents the effect of a simple uni-univalent salt with a common ion, calculated by assuming complete dissociation of the salt. The salts with a common ion decrease the solubility to nearly the same extent, and are in approximate agreement with the values computed on the basis of the simple solubility product principle. Fig. 1-2 shows graphically some selected results for silver sulphate. The addition, in moderate concentrations, of a common univalent ion, like Ag^+, is in approximate agreement with the simple theory, but no such agreement is obtained by the addition of a common divalent ion, like SO_4^{--}. A striking fact that emerges from these studies is that the solubility increases in most cases upon the addition of electrolytes with *no common ion* ; we may term this influence the **salt effect.** Furthermore, it was found that the salt effect depends upon the valency of the ions of the precipitate and upon the nature of the added electrolyte ; usually it increases markedly with increasing valency of the ions of the precipitate. The addition of a salt with no common ion will increase the ionic strength of the solution and hence decrease the activity coefficients of both ions of the sparingly soluble salt ; the solubility of the latter must increase in order that the activity product, $[M^+] . [A^-] . f_{M^+} . f_{A^-}$, may be kept constant. It can be shown on the basis of the Debye-Hückel-Onsager theory that for aqueous solutions at 25°C :

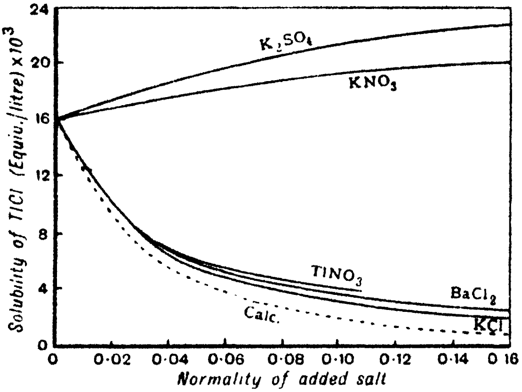

FIG. 1-1.—Influence of various salts on the solubility of TlCl

$$\log f_i = - \frac{0{\cdot}505 z_i^2 . \mu^{0{\cdot}5}}{1 + 3{\cdot}3 \times 10^7 a . \mu^{0{\cdot}5}},$$

where f_i is the activity coefficient of the ion, z_i is the valency of the ion concerned, μ is the ionic strength of the solution (Section **I, 5**), and a is the average " effective diameter " of all the ions in the solution. For very dilute solutions ($\mu^{0{\cdot}5} < 0{\cdot}1$) the second term of the denominator is negligible and the equation reduces to :

$$\log f_i = - 0{\cdot}505 z_i^2 . \mu^{0{\cdot}5}.$$

For more concentrated solutions ($\mu^{0{\cdot}5} > 0{\cdot}3$) an additional term $B\mu$ is added to the equation ; B is an empirical constant. For a more detailed treatment of the influence of salts upon solubility and solubility product, particularly of the work of Brönsted and of La Mer, the reader is referred to text-books of electrochemistry.*

It will be clear from the above short discussion that two factors may come into play when a solution of a salt containing a common ion is added to a saturated solution of a slightly soluble salt. At moderate concentrations of the added salt, the solubility will generally decrease, but with higher concentrations when the ionic strength of the solution increases considerably and the activity coefficients of the ions decrease, the solubility may actually increase. This is one of the reasons, provided complex ion formation is absent, why a very large excess of the precipitating agent is avoided in quantitative analysis.

I, 11. Fractional precipitation.—We have thus far considered the solubility product principle in connexion with the precipitation of one sparingly soluble salt. We shall now extend our studies to the case where two slightly soluble salts may be formed. For simplicity, we shall study the situation which arises when a precipitating agent is added to a solution containing two anions, both of which form slightly soluble salts with the same cation, *e.g.*, when silver nitrate solution is added to a solution containing both chloride and iodide ions. The questions which arise are : which salt will be precipitated first, and how completely will the first salt be precipitated before the second ion begins to react with the reagent ?

The solubility products of silver chloride and silver iodide are respectively $1{\cdot}2 \times 10^{-10}$ and $1{\cdot}7 \times 10^{-16}$;

$$i.e., \quad [Ag^+] \times [Cl^-] = 1{\cdot}2 \times 10^{-10} \qquad \text{(i)},$$

$$[Ag^+] \times [I^-] = 1{\cdot}7 \times 10^{-16} \qquad \text{(ii)}.$$

It is evident that silver iodide being less soluble will be precipitated first since its solubility product will be first exceeded. Silver chloride will be precipitated when the Ag^+ ion concentration is greater than

$$\frac{S_{AgCl}}{[Cl^-]} = \frac{1{\cdot}2 \times 10^{-10}}{[Cl^-]},$$

and then both salts will be precipitated simultaneously. When silver chloride commences to precipitate, silver ions will be in equilibrium with both salts and equations (i) and (ii) will be simultaneously satisfied, or

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* See, for example, S. Glasstone, *The Electrochemistry of Solutions*, 1937, p. 127 (Methuen and Co.).

$$[\mathrm{Ag}^+] = \frac{S_{\mathrm{AgI}}}{[\mathrm{I}^-]} = \frac{S_{\mathrm{AgCl}}}{[\mathrm{Cl}^-]} \qquad \text{(iii)},$$

$$\text{and } \frac{[\mathrm{I}^-]}{[\mathrm{Cl}^-]} = \frac{S_{\mathrm{AgI}}}{S_{\mathrm{AgCl}}} = \frac{1{\cdot}7 \times 10^{-16}}{1{\cdot}2 \times 10^{-10}} = \frac{1}{7{\cdot}1 \times 10^{7}} \qquad \text{(iv)}.$$

Hence when the concentration of the iodide ion is about one millionth part of the chloride ion concentration, silver chloride will be precipitated. If the initial concentration of both chloride and iodide ions is $0{\cdot}1N$, then silver chloride will be precipitated when

$[\mathrm{I}^-] = 0{\cdot}1 / 7{\cdot}1 \times 10^7 = 1{\cdot}4 \times 10^{-7}N = 1{\cdot}8 \times 10^{-5}$ g. per litre.

Thus an almost complete separation is theoretically possible. The separation is feasible in practice if the point at which the iodide precipitation is complete can be detected. This may be done: (*a*) by the use of an absorption indicator (see Section **I, 41C**), or (*b*) by a potentiometric method with a silver electrode (see Section **I, 53**).

For a mixture of bromide and iodide:

$$\frac{[\mathrm{I}^-]}{[\mathrm{Br}^-]} = \frac{S_{\mathrm{AgI}}}{S_{\mathrm{AgBr}}} = \frac{1{\cdot}7 \times 10^{-16}}{3{\cdot}5 \times 10^{-13}} = \frac{1}{2{\cdot}0 \times 10^{3}}$$

Precipitation of silver bromide will occur when the concentration of the bromide ion in the solution is $2{\cdot}0 \times 10^3$ times that of the iodide concentration. The separation is therefore not quite so complete as in the case of chloride and iodide, but can nevertheless be effected with fair accuracy with the aid of adsorption indicators (Sections **I, 41C** and **III, 29**).

I, 12. Complex ions.—The increase in solubility of a precipitate upon the addition of excess of the precipitating agent is frequently due to the formation of a complex ion. A **complex ion** is formed by the union of a simple ion with either other ions of opposite charge or with neutral molecules. Let us examine a few examples in detail.

When potassium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide is first formed because the solubility product of silver cyanide,

$$[\mathrm{Ag}^+] \times [\mathrm{CN}^-] \leftarrow S_{\mathrm{AgCN}} \qquad \text{(i)},$$

is exceeded. The reaction is expressed:

$$\mathrm{K}^+ + \mathrm{CN}^- + \mathrm{Ag}^+ + \mathrm{NO}_3^- = \mathrm{AgCN} + \mathrm{K}^+ + \mathrm{NO}_3^-,$$

or

$$\mathrm{CN}^- + \mathrm{Ag}^+ = \mathrm{AgCN}.$$

The precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion $[Ag(CN)_2]^-$ being produced:

$$AgCN\ (solid) + CN^-\ (excess) \rightleftharpoons [Ag(CN)_2]^{-}\text{*}$$

$$(or\ AgCN + KCN = K[Ag(CN)_2]\text{—a soluble complex salt}).$$

This complex ion dissociates to give silver ions, since the addition of sulphide ions yields a precipitate of silver sulphide (solubility product $1{\cdot}6 \times 10^{-49}$), and also silver is precipitated from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^- \qquad \text{(ii).}$$

By applying the law of mass action to (ii), we obtain the dissociation constant or instability constant of the complex ion:

$$\frac{[Ag^+] \times [CN^-]^2}{[\{Ag(CN)_2\}^-]} = K \qquad \text{(iii).}$$

The constant has a value of $1{\cdot}0 \times 10^{-21}$ at the ordinary temperature. By inspection of this expression, and bearing in mind that excess of cyanide ion is present, it should be evident that the silver ion concentration must be very small, so small in fact that the solubility product of silver cyanide is not exceeded.

Consider now a somewhat different type of complex ion formation, *viz.*, the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reactions are:

$$Ag^+ + Cl^- \rightleftharpoons AgCl;$$

$$AgCl\ (solid) \rightleftharpoons Ag^+ + Cl^- + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

$$(or\ AgCl + 2NH_3 = [Ag(NH_3)_2]Cl).$$

Here again, for reasons similar to those already given, silver ions are present in solution. The dissociation of the complex ion is represented by:

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3,$$

and the instability constant is given by:

$$\frac{[Ag^+] \times [NH_3]^2}{[\{Ag(NH_3)_2\}^+]} = K = 6{\cdot}8 \times 10^{-8}.$$

---

[*] It is usual to employ square brackets to include the whole of a complex ion. In order to avoid confusion with concentrations for which square brackets are also widely used, concentrations will be represented in heavy type and complex ions either in lighter type or between curly brackets.

The magnitude of the instability constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the **dissociation or instability constant.** The more stable the complex, the smaller is the instability constant, *i.e.*, the smaller is the tendency of the complex ion to dissociate into its constituent ions. When the complex ion is very stable, *e.g.*, the ferrocyanide ion $[Fe(CN)_6]^{----}$, the ordinary ionic reactions of the components are not shown. A few selected values of these constants at the ordinary temperature, determined by methods involving potentiometric titration (Sections **I, 51–53**), are collected in Table V; this is instructive and also useful for reference purposes.

TABLE V. INSTABILITY CONSTANTS OF COMPLEX IONS

$\frac{[Ag^+] \times [NH_3]^2}{[\{Ag(NH_3)_2\}^+]} = 6{\cdot}8 \times 10^{-8}$	$\frac{[Cd^{++}] \times [CN^-]^4}{[\{Cd[CN)_4\}^{--}]} = 1{\cdot}4 \times 10^{-17}$
$\frac{[Ag^+] \times [S_2O_3^{--}]^2}{[\{Ag(S_2O_3)_2\}^{---}]} = 1{\cdot}0 \times 10^{-13}$	$\frac{[Hg^{++}] \times [Cl^-]^4}{[\{HgCl_4\}^{--}]} = 6{\cdot}0 \times 10^{-17}$
$\frac{[Ag^+] \times [CN^-]^2}{[\{Ag(CN)_2\}^-]} = 1{\cdot}0 \times 10^{-21}$	$\frac{[Hg^{++}] \times [I^-]^4}{[\{HgI_4\}^{--}]} = 5{\cdot}0 \times 10^{-31}$
$\frac{[Cu^+] \times [CN^-]^4}{[\{Cu(CN)_4\}^{---}]} = 5{\cdot}0 \times 10^{-28}$	$\frac{[Hg^{++}] \times [CN^-]^4}{[\{Hg(CN)_4\}^{--}]} = 4{\cdot}0 \times 10^{-42}$

The application of complex ion formation in chemical separations depends upon the fact that one component may be transformed into a complex ion which is no longer precipitable with the precipitating agent, whereas another component is precipitated. One example may be mentioned here. This is concerned with the separation of cadmium and copper. Excess of potassium cyanide solution is added to the solution containing the two salts when the complex ions $[\{Cd(CN)_4]^{--}$ and $[Cu(CN)_4]^{---}$ respectively are formed. Upon passing hydrogen sulphide into the solution containing excess of CN^- ions, a precipitate of cadmium sulphide is produced. Despite the higher solubility product of CdS (3·6 × 10^{-29} as against 8·5 × 10^{-45} for copper sulphide), the former is precipitated because the complex cadmium cyanide ion has a greater instability constant (see Table V).

I, 13. Effect of acids upon the solubility of a precipitate.—For sparingly soluble salts of a strong acid the effect of the addition of an acid will be similar to that of any other indifferent electrolyte (compare salt effect in Section **I, 10**). If the sparingly soluble salt MA is the salt of a weak acid HA, then acids will, in general, have a solvent effect upon it. Let us suppose that hydrochloric acid is added to an aqueous suspension of such a salt. The following equilibrium will be established :

$$M^+ + A^- + H^+ + Cl^- \rightleftharpoons HA + M^+ + Cl^-.$$

If the dissociation constant of the acid HA is very small, the anion A^- will be removed from the solution to form the undissociated acid HA. Consequently more of the salt will pass into solution to replace the anions removed in this way and this process will continue until equilibrium is established (*i.e.*, until $[M^+] \times [A^-]$ has become equal to the solubility product of MA) or, if sufficient hydrochloric acid is present, until the sparingly soluble salt has dissolved completely. Similar reasoning may be applied to salts of polybasic acids, such as phosphoric acid ($K_1 = 7{\cdot}5 \times 10^{-3}$; $K_2 = 6{\cdot}2 \times 10^{-8}$; $K_3 = 5 \times 10^{-13}$), oxalic acid ($K_1 = 5{\cdot}9 \times 10^{-2}$; $K_2 = 6{\cdot}4 \times 10^{-5}$), and arsenic acid. Thus the solubility of, say, silver orthophosphate is due to the removal of the PO_4^{---} ion as HPO_4^{--} and/or $H_2PO_4^-$:

$$PO_4^{---} + H^+ \rightleftharpoons HPO_4^{--};$$
$$HPO_4^{--} + H^+ \rightleftharpoons H_2PO_4^-.$$

With weak acids, such as carbonic ($K_1 = 4{\cdot}3 \times 10^{-7}$; $K_2 = 5{\cdot}6 \times 10^{-11}$), sulphurous ($K_1 = 1{\cdot}7 \times 10^{-2}$; $K_2 = 1{\cdot}0 \times 10^{-7}$), and nitrous ($K_1 = 4{\cdot}6 \times 10^{-4}$) acids, an additional factor contributing to the increased solubility is the actual disappearance of the acid from solution either spontaneously or on gentle warming. An explanation is thus provided for the well-known solubility of the sparingly soluble sulphites, carbonates, oxalates, phosphates, arsenites, arsenates, acetates, cyanides (with the exception of silver cyanide, which is actually a salt of the strong acid $H[Ag(CN)_2]$), fluorides, and salts of other organic acids in strong acids.

The sparingly soluble sulphates (*e.g.*, those of barium, strontium, and lead) also exhibit increased solubility in acids as a consequence of the weakness of the second stage of ionisation of sulphuric acid ($K_2 = 1{\cdot}2 \times 10^{-2}$); the first stage is completely ionised :

$$Ba^{++} + SO_4^{--} + H^+ + Cl^- \rightleftharpoons HSO_4^- + Ba^{++} + Cl^-.$$

Since K_2 is comparatively large, the solvent effect is relatively small. However, in the quantitative separation of barium sulphate, precipitation is usually carried out in slightly acid solution in order to obtain a more easily filterable precipitate and to reduce coprecipitation (Section **I, 58**).

The precipitation of substances within a controlled range of *p*H is discussed in Section **I, 61B.**

I, 14. Effect of temperature upon the solubility of a precipitate.—The solubility of the precipitates encountered in quantitative analysis increases with rise of temperature. With some substances the influence of temperature is small, but with others it is quite appreciable. Thus the solubility of silver chloride at 10° and 100°C is 1·72 and 21·1 mg. per litre respectively, whilst that of barium sulphate at these two temperatures is 2·2 and 3·9 mg. per litre respectively. In many instances, the common ion effect reduces the solubility to so small a value that the temperature effect, which is otherwise appreciable, becomes very small. Wherever possible it is advantageous to filter while the solution is hot; the rate of filtration is increased as is also the solubility of foreign substances, thus rendering their removal from the precipitate more complete. The double phosphates of ammonium with magnesium, manganese or zinc as well as lead sulphate and silver chloride are usually filtered at the laboratory temperature to avoid solubility losses.

I, 15. Effect of the solvent upon the solubility of a precipitate.—The solubility of most inorganic compounds is reduced by the addition of organic solvents, such as methyl, ethyl and *n*-propyl alcohols, acetone, etc. For example, the addition of about 20 per cent. by volume of ethyl alcohol renders the solubility of lead sulphate practically negligible, thus permitting quantitative separation. Similarly calcium sulphate separates quantitatively from 50 per cent. ethyl alcohol. Other examples of the influence of solvent will be found in Chapter IV.

I, 16. The ionic product of water.—Kohlrausch and Heydweiller (1894) found that the most highly purified water that can be obtained possesses a small but definite conductivity. Water must therefore be slightly ionised in accordance with the equation: $H_2O \rightleftharpoons H^+ + OH^-$*.

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* Strictly speaking the hydrogen ion H^+ exists in water as the hydroxonium ion H_3O^+. The electrolytic dissociation of water should therefore be written:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-.$$

For the sake of simplicity, the more familiar symbol H^+ will be retained.

Applying the law of mass action to this equation, we obtain, for any given temperature :

$$\frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}} = \frac{[H^+] . [OH^-]}{[H_2O]} \times \frac{f_{H^+} \cdot f_{OH^-}}{f_{H_2O}} = \text{a constant,}$$

where a_x, $[x]$, and f_x refer to the activity, concentration and activity coefficient of the species x. Since water is only slightly ionised, the ionic concentrations will be small and their activity coefficients may be regarded as unity ; the activity of the unionised molecules may also be taken as unity. The expression thus becomes :

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant.}$$

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant. Hence :

$$[H^+] \times [OH^-] = K_w,$$

where K_w is the **ionic product of water.** It must be pointed out that the assumption that the activity coefficients of the ions are unity and that the activity coefficient of water is constant applies strictly to pure water and to very dilute solutions (ionic strength $< 0{\cdot}01$) ; in more concentrated solutions, *i.e.*, in solutions of appreciable ionic strength, the electrical environment affects the activity coefficients of the ions (compare Section **I, 10**) and also the activity of the unionised water. The ionic product of water will then not be constant, but will depend upon the ionic environment. It is, however, difficult to determine the activity coefficients, except under specially selected conditions, so that in practice the ionic product K_w, although not strictly constant, is employed.

The ionic product varies with the temperature, but under ordinary experimental conditions (at about 25°C) its value may be taken as 1×10^{-14} with concentrations expressed in gram ions per litre. This is sensibly constant in dilute aqueous solutions. If the product of $[H^+]$ and $[OH^-]$ in aqueous solution momentarily exceeds this value, the excess ions will immediately combine to form water. Similarly if the product of the two ionic concentrations is momentarily less than 10^{-14}, more water molecules will dissociate until the equilibrium value is attained.

The hydrogen and hydroxyl ion concentrations are equal in pure water; therefore $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ gram ions per litre at about 25°C. A solution in which the hydrogen and hydroxyl ion concentrations are equal is termed an exactly **neutral solution**. If $[H^+]$ is greater than 10^{-7}, the solution is **acid**, and if less than 10^{-7}, the solution is **alkaline** (or **basic**). It follows that at ordinary temperatures $[OH^-]$ is greater than 10^{-7} in alkaline solution and less than this value in acid solution.

In all cases the reaction of the solution can be quantitatively expressed by the magnitude of the hydrogen ion (or hydroxonium ion) concentration, or, less frequently, of the hydroxyl ion concentration, since the following simple relations between $[H^+]$ and $[OH^-]$ exist:

$$[H^+] = \frac{K_w}{[OH^-]}, \text{ and } [OH^-] = \frac{K_w}{[H^+]}.$$

The variation of K_w with temperature is shown in Table VI.

TABLE VI. IONIC PRODUCT OF WATER AT VARIOUS TEMPERATURES.

Temp. (°C)	$K_w \times 10^{14}$	*Temp.* (°C)	$K_w \times 10^{14}$
0°	0·12	35°	2·09
5°	0·19	40°	2·92
10°	0·29	45°	4·02
15°	0·45	50°	5·48
20°	0·68	55°	7·30
25°	1·01	60°	9·62
30°	1·47		

I, 17. The hydrogen ion exponent, *p*H.—For many purposes, especially when dealing with small concentrations, it is cumbersome to express concentrations of hydrogen and hydroxyl ions in terms of gram equivalents per litre. A very convenient method was proposed by S. P. L. Sörensen (1909). He introduced the **hydrogen ion exponent** *p*H defined by the relationships:

$$pH = -\log_{10}[H^+] = \log_{10} 1/[H^+], \text{ or } [H^+] = 10^{-pH}.$$

The quantity *p*H is thus the logarithm (to the base 10) of the reciprocal of the hydrogen ion concentration, or is equal to the logarithm of the hydrogen ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions molar (or normal) with respect to hydrogen and hydroxyl ions can be expressed by a series of positive numbers between 0 and 14. Thus a neutral solution with $[H^+] = 10^{-7}$ has a *p*H of 7; a solution with molar (or normal) concentration of hydrogen ions has a *p*H of 0 ($= 10^0$); and a solution molar with respect to hydroxyl ions has $[H^+] = K_w / [OH^-] = 10^{-14}/10^0 = 10^{-14}$, and possesses a *p*H of 14. A neutral solution is therefore one in which $pH = 7$, an acid solution one in which $pH < 7$, and an alkaline solution one in which $pH > 7$. An alternative definition for a neutral solution, applicable to all temperatures, is one in which the hydrogen ion and hydroxyl ion concentrations are equal. In an acid solution the hydrogen ion concentration exceeds the hydroxyl ion concentration, whilst in an alkaline or basic solution, the hydroxyl ion concentration is greater.

Example 10. (i) Find the *p*H of a solution of which $[H^+] = 4{\cdot}0 \times 10^{-5}$.

Log $4{\cdot}0 = 0{\cdot}602$, hence log $4{\cdot}0 \times 10^{-5}$ is $\bar{5}{\cdot}602 = 0{\cdot}602 - 5 = -4{\cdot}398$

(the decimal part or mantissa of the logarithm is always positive).

$$pH = -\log [H^+] = -(-4{\cdot}398) = \mathit{4{\cdot}398}.$$

(ii) Find the hydrogen ion concentration corresponding to $pH = 5{\cdot}643$.

$$pH = -\log [H^+] = 5{\cdot}643 ;\ \therefore \log [H^+] = -5{\cdot}643.$$

This must be written in the usual form containing a negative characteristic and a positive mantissa:

$$\log [H^+] = -5{\cdot}643 = \bar{6}{\cdot}357.$$

Referring to a table of antilogarithms, the number corresponding to the logarithm of 0·357 is 2·28; the number corresponding to the logarithm $\bar{6}{\cdot}357$ is accordingly $2{\cdot}28 \times 10^{-6}$.

$[H^+]$ is therefore $\mathit{2{\cdot}28} \times \mathit{10^{-6}}$.

(iii) Calculate the *p*H of a 0·01 molar solution of acetic acid (the degree of dissociation is 12·5%).

The hydrogen ion concentration is $0{\cdot}125 \times 0{\cdot}01 = 1{\cdot}25 \times 10^{-3}$. Now log $1{\cdot}25 = 0{\cdot}097$;

$$pH = -(-3 + 0{\cdot}097) = \mathit{2{\cdot}903}.$$

The hydroxyl ion concentration may be expressed in a similar way:

$$pOH = -\log_{10} [OH^-] = \log_{10} 1/[OH^-], \text{ or } [OH^-] = 10^{-\,OH}.$$

If we write the equation :

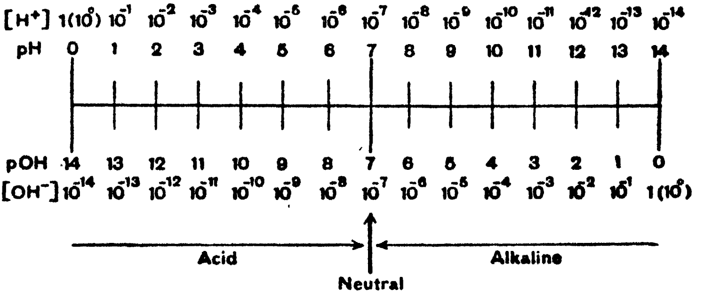
$$[H^+] \times [OH^-] = K_w = 10^{-14},$$

in the form :

$$\log [H^+] + \log [OH^-] = \log K_w = -14,$$
$$\text{then } pH + pOH = pK_w = 14.$$

This relationship should hold for all dilute solutions at about 25°C.

Fig. 1-3 will serve as a useful mnemonic for the relation between $[H^+]$, pH, $[OH^-]$ and pOH in acid and alkaline solution.



[H⁺] 1(10⁰) 10⁻¹ 10⁻² 10⁻³ 10⁻⁴ 10⁻⁵ 10⁻⁶ 10⁻⁷ 10⁻⁸ 10⁻⁹ 10⁻¹⁰ 10⁻¹¹ 10⁻¹² 10⁻¹³ 10⁻¹⁴
pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pOH 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
[OH⁻] 10⁻¹⁴ 10⁻¹³ 10⁻¹² 10⁻¹¹ 10⁻¹⁰ 10⁻⁹ 10⁻⁸ 10⁻⁷ 10⁻⁶ 10⁻⁵ 10⁻⁴ 10⁻³ 10⁻² 10⁻¹ 1(10⁰)
Acid
Alkaline
Neutral

FIG. 1-3.

The logarithmic or exponential method has also been found useful for expressing other small quantities which arise in quantitative analysis. These include (i) dissociation constants (Section **I, 4**), (ii) other ionic concentrations, and (iii) solubility products (Section **I, 8**).

(i) For any acid with a dissociation constant of K_a :

$$pK_a = -\log K_a = 1/\log K_a.$$

Similarly for any base with dissociation constant K_b :

$$pK_b = -\log K_b = 1/\log K_b.$$

(ii) For any ion I of concentration [I] :

$$pI = -\log [I] = 1/\log [I].$$

Thus for $[Na^+] = 8 \times 10^{-5}, pI = 4{\cdot}1$.

(iii) For a salt with a solubility product S :

$$pS = -\log S = 1/\log S.$$

I, 18. The hydrolysis of salts.—Salts may be divided into four main groups :

I. those derived from the strong acids and strong bases, *e.g.*, potassium chloride ;

II, those derived from weak acids and strong bases, *e.g.*, sodium acetate ;

III, those derived from strong acids and weak bases, *e.g.*, ammonium chloride ; and

IV, those derived from weak acids and weak bases, *e.g.*, ammonium formate or aluminium acetate.

When any of these is dissolved in water, the solution, as is well known, is not always neutral in reaction. Interaction occurs with the ions of water and the resulting solution may be neutral, acid or alkaline according to the nature of the salt.

With an aqueous solution of a salt of group I, neither the anions have any tendency to combine with the hydrogen ions nor the cations with the hydroxyl ions of water since the related acids and bases are strong electrolytes. The equilibrium between the hydrogen and hydroxyl ions in water :

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{(i)},$$

is therefore not disturbed and the solution remains neutral.

Consider, however, a salt MA derived from a weak acid HA and a strong base BOH (group II). The salt is completely dissociated in aqueous solution :

$$MA \rightleftharpoons M^+ + A^-.$$

A very small concentration of hydrogen and hydroxyl ions, originating from the small but finite ionisation of water, will be initially present. HA is a weak acid, that is, it is dissociated only to a small degree ; the concentration of A^- ions which can exist in equilibrium with H^+ ions is accordingly small. In order to maintain the equilibrium, the large initial concentration of A^- ions must be reduced by combination with H^+ ions to form undissociated HA :

$$H^+ + A^- \rightleftharpoons HA \qquad \text{(ii)}.$$

The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water ; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA, consequently the hydroxyl ion concentration of the solution will increase and the solution will react alkaline. The net result is that the anions of the salt react with the hydrogen ions of the water yielding the weak acid HA, and there is an increase in the concentration of hydroxyl ions over that present in water.

It is usual in writing equations involving equilibria between completely dissociated and slightly dissociated or sparingly soluble substances to employ the ions of the former and the molecules of the latter. The reaction is therefore written :

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad \text{(iii)}.$$

This equation can also be obtained by combining (i) and (ii) since both equilibria must coexist.

This interaction between the ion (or ions) of a salt and the ions of water is called **hydrolysis.** Formerly the chemical reaction was written :

$$MA + H_2O \rightleftharpoons MOH + HA,$$

or as : $\quad$ *Salt* + *Water* ⇌ *Base* + *Acid.*

The reaction of the solution was clearly dependent upon the relative strengths of MOH and HA. This led to the definition of hydrolysis as the decomposition of a salt into an acid and a base.

Let us now study the salt of a strong acid and a weak base (group III). Here the initial high concentration of cations M^+ will be reduced by combination with the hydroxyl ions of water to form the little dissociated base MOH until the equilibrium :

$$M^+ + OH^- \rightleftharpoons MOH \qquad \text{(iv)},$$

is attained. The hydrogen ion concentration of the solution will thus be increased and the solution will react acid. The hydrolysis is here represented by :

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(v)}.$$

For salts of group IV in which both the acid and the base are weak, two reactions will occur simultaneously :

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(vi)},$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \text{(vii)}.$$

The reaction of the solution will clearly depend upon the relative dissociation constants of the acid and the base. If they are equal in strength, the solution will be neutral ; if $K_a > K_b$, it will be acid, and if $K_b > K_a$, it will be alkaline.

Having considered all the possible cases, we are now in a position to give a more general definition of hydrolysis. **Hydrolysis** is the interaction between the ion (or ions) of a salt and the ions of water with the production of (*a*) a weak acid or a weak base, or (*b*) of both a weak acid and a weak base.

I, 19. Hydrolysis constant and degree of hydrolysis.—Case I. Salt of a weak acid and a strong base. The equilibrium in a solution of a salt MA may be represented by :

$$M^+ + A^- + H_2O \rightleftharpoons M^+ + OH^- + HA,$$

or by
$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad \text{(i)}.$$

Applying the law of mass action, we obtain :

$$\frac{a_{OH^-} \times a_{HA}}{a_{A^-}} = \frac{[OH^-] \, . \, [HA]}{[A^-]} \times \frac{f_{OH^-} \cdot f_{HA}}{f_{A^-}} = K_h \qquad \text{(ii)},$$

where a, f, and [ ] refer to activities, activity coefficients and concentrations respectively, and K_h is the **hydrolysis constant.** The solution is assumed to be dilute ; the activity of the unionised water may be taken as constant. In dilute solutions, the ionic strength is small, and the approximation that the activity coefficient of the unionised acid is unity and that both ions have the same activity coefficient may be introduced. Equation (ii) then reduces to :

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} \qquad \text{(iii)}.$$

This is often written in the form :

$$K_h = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed salt}]} \qquad \text{(iv)} ;$$

the free strong base and the unhydrolysed salt are completely dissociated and the acid is very little dissociated.

The **degree of hydrolysis** is the fraction of each gram molecule hydrolysed at equilibrium. Let 1 gram mol of salt be dissolved in V litres of solution and let x be the degree of hydrolysis. The concentrations in gram mols or gram ions per litre are :

$$\underset{(1-x)/V}{A^-} + H_2O \rightleftharpoons \underset{x/V}{OH^-} + \underset{x/V}{HA}$$

Substituting these values in (iii) :

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{x/V \times x/V}{(1-x)/V} = \frac{x^2}{(1-x)V} \qquad \text{(v)}.$$

This expression enables us to calculate the degree of hydrolysis from the value of the hydrolysis constant at the dilution V. It is evident that as V increases, the degree of hydrolysis x must increase.

The two equilibria :

$$H_2O \rightleftharpoons H^+ + OH^-,$$

and $$HA \rightleftharpoons H^+ + A^-,$$

must coexist with the hydrolytic equilibrium :

$$A^- + H_2O \rightleftharpoons HA + OH^-.$$

Hence the two relationships :

$$[H^+] \times [OH^-] = K_w$$

and $$[H^+] \times [A^-] \,/\, [HA] = K_a.$$

must hold in the same solution as :

$$[OH^-] \times [HA] \,/\, [A^-] = K_h.$$

But $$\frac{K_w}{K_a} = \frac{[H^+] \times [OH^-] \times [HA]}{[H^+] \times [A^-]} = \frac{[OH^-] \times [HA]}{[A^-]} = K_h,$$

therefore $$K_w/K_a = K_h \qquad \text{(vi)},$$

or $$pK_h = pK_w - pK_a \qquad \text{(vii)}.$$

The hydrolysis constant is thus related to the ionic product of the water and the ionisation constant of the acid. Since K_a varies slightly and K_w varies considerably with temperature, K_h and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

Example 11. Calculate (i) the hydrolysis constant, (ii) the degree of hydrolysis, and (iii) the hydrogen ion concentration of a 0·01 molar solution of sodium acetate at the laboratory temperature.

$$K_h = \frac{K_w}{K_a} = \frac{1{\cdot}0 \times 10^{-14}}{1{\cdot}82 \times 10^{-5}} = 5{\cdot}5 \times 10^{-10}.$$

The degree of hydrolysis x is given by :

$$K_h = \frac{x^2}{(1 - x)V}\,.$$

Substituting for K_h and V $(= 1/c)$, we obtain :

$$5{\cdot}5 \times 10^{-10} = \frac{x^2 \times 0{\cdot}01}{(1 - x)}\,.$$

Solving this quadratic equation for x, $x = 0{\cdot}000235$ or $0{\cdot}0235\%$.

$$\underset{(1-x)\text{ mols}}{C_2H_3O_2^-} + H_2O \rightleftharpoons \underset{x\text{ mols}}{H.C_2H_3O_2} + \underset{x\text{ mols}}{OH^-}.$$

If the solution were completely hydrolysed, the concentration of acetic acid produced would be $0{\cdot}01M$. But the degree of hydrolysis is $0{\cdot}0235\%$, therefore the concentration of acetic acid is $2{\cdot}35 \times 10^{-6}$

M. This is also equal to the hydroxyl ion concentration produced, *i.e.*, $pOH = 5{\cdot}63$.

$$pH = 14{\cdot}0 - 5{\cdot}63 = 8{\cdot}37.$$

The pH may also be computed from equation (ix) below :

$$\begin{aligned} pH &= 1/2\, pK_w + 1/2\, pK_a + 1/2 \log c, \\ &= 7{\cdot}0 \quad + 2{\cdot}37 \quad + 1/2\,(-2) = 8{\cdot}37. \end{aligned}$$

The hydrogen ion concentration of a solution of a hydrolysed salt can be readily computed. The amounts of HA and OH^- ions formed as a result of hydrolysis are equal, therefore in a solution of the pure salt in water $[HA] = [OH^-]$. If the concentration of the salt is *c* gram mols per litre, then :

$$\frac{[HA] \times [OH^-]}{[A^-]} = \frac{[OH^-]^2}{c} = K_h = \frac{K_w}{K_a},$$

and $$[OH^-] = \sqrt{c.\, K_w \,/\, K_a} \qquad \text{(vii)},$$

or $$[H^+] = \sqrt{K_w \,.\, K_a \,/\, c}, \text{ since } [H^+] = K_w \,/\, [OH^-] \qquad \text{(viii)};$$

$$pH = 1/2\, pK_w + 1/2\, pK_a + 1/2 \log c\,^* \qquad \text{(ix)}.$$

Equation (ix) can be employed for the calculation of the pH of a solution of a salt of a weak acid and a strong base. Thus the pH of a $0{\cdot}05N$ solution of sodium benzoate is given by :

$$pH = 7{\cdot}0 + 2{\cdot}10 + 1/2(-1{\cdot}30) = 8{\cdot}45.$$

(Benzoic acid : $K_a = 6{\cdot}37 \times 10^{-5}$; $pK_a = 4{\cdot}20$.)

Such a calculation will provide useful information as to the indicator which should be employed in the titration of a weak acid and a strong base (see Section **I, 33**).

Case 2. Salt of a strong acid and a weak base. The hydrolytic equilibrium is represented by :

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{(x)}.$$

By applying the law of mass action along the lines of **Case 1**, the following equations are obtained :

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[\text{Acid}] \times [\text{Base}]}{[\text{Unhydrolysed Salt}]} = \frac{K_w}{K_b} \qquad \text{(xi)},$$

$$= \frac{x^2}{(1-x)V} \qquad \text{(xii)}.$$

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* To be consistent we should write $p_c = -\log c$.

K_b is the dissociation constant of the base. Furthermore, since [MOH] and [H⁺] are equal (equation (x),

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[H^+]^2}{c} = \frac{K}{K_b},$$

$$[H^+] = \sqrt{c.K_w / K_b},$$

or $$pH = 1/2pK_w - 1/2\, pK_b - 1/2 \log c \qquad \text{(xiii)}.$$

Equation (xiii) may be applied to the calculation of the pH of solutions of salts of strong acids and weak bases. Thus the pH of a $0{\cdot}02N$ solution of ammonium chloride is :

$$pH = 7{\cdot}0 - 2{\cdot}37 - 1/2\,(-0{\cdot}70) = 4{\cdot}98.$$

(Ammonium hydroxide : $K_b = 1{\cdot}85 \times 10^{-5}$; $pK_b = 4{\cdot}74$.)

Case 3. Salt of a weak acid and a weak base. The hydrolytic equilibrium is expressed by the equation :

$$M^+ + A^- + H_2O \rightleftharpoons MOH + HA \qquad \text{(xiv)}.$$

Applying the law of mass action and taking the activity of unionised water as unity, we have :

$$K_h = \frac{a_{MOH} \times a_{HA}}{a_{M^+} \times a_{A^-}} = \frac{[MOH]\,.\,[HA]}{[M^+]\,.\,[A^-]} \times \frac{f_{MOH}\,.\,f_{HA}}{f_{M^+}\,.\,f_{A^-}} \qquad \text{(xv)}.$$

By the usual approximations, that is, by assuming that the activity coefficients of the unionised molecules and, less justifiably, of the ions are unity, the following approximate equation is obtained :

$$K_h = \frac{[MOH] \times [HA]}{[M^+] \times [A^-]} \qquad \text{(xvi)},$$

$$= \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed Salt}]^2} \qquad \text{(xvii)}.$$

If x is the degree of hydrolysis of 1 gram mol of the salt dissolved in V litres of solution, then the individual concentrations are :

$$[MOH] = [HA] = x/V\,;\ [M^+] = [A^-] = (1 - x)/V.$$

Substituting these values in (xvi) :

$$K_h = \frac{x/V\,.\,x/V}{(1-x)/V.(1-x)/V} = \frac{x^2}{(1-x)^2} \qquad \text{(xviii)}.$$

The degree of hydrolysis and consequently the pH is independent of the concentration of the solution.*

As in **Case 1** the expressions :

$$K_w = [\mathrm{H}^+] \times [\mathrm{OH}^-],$$

$$K_a = \frac{[\mathrm{H}^+] \times [\mathrm{A}^-]}{[\mathrm{HA}}, \text{ and } K_b = \frac{[\mathrm{M}^+] \times [\mathrm{OH}^-]}{[\mathrm{MOH}]},$$

hold simultaneously with equation (xiv) for the hydrolytic equilibrium. By substitution in the last-named equation, it can be readily shown that :

$$K_h = K_w \,/\, K_a \times K_b \qquad \text{(xix)},$$

or

$$pK_h = pK_w - pK_a - pK_b \qquad \text{(xx)}.$$

This expression enables us to compute the value of the degree of hydrolysis x from the dissociation constants of the acid and the base.

The hydrogen ion concentration of the hydrolysed solution is calculated in the following manner :

$$[\mathrm{H}^+] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = K_a \times \frac{x/V}{(1-x)/V} = K_a \times \frac{x}{(1-x)}.$$

But $x/(1 - x) = \sqrt{K_h}$ (by equation (xviii)),

hence $$[\mathrm{H}^+] = K_a \cdot \sqrt{K_h} = \sqrt{K_w \times K_a / K_b} \qquad \text{(xxi)},$$

or $$p\mathrm{H} = 1/2\, pK_w + 1/2\, pK_a - 1/2\, pK_b \qquad \text{(xxii)}.$$

If the ionisation constants of the acid and the base are equal, that is, $K_a = K_b$, $pH = 1/2\, pK_w = 7{\cdot}0$, and the solution is neutral although hydrolysis may be considerable. If $K_a > K_b$, $p\mathrm{H} < 7$ and the solution is acid, but when $K_b > K_a$, $p\mathrm{H} > 7$ and the solution reacts alkaline.

The pH of a solution of ammonium acetate is given by :

$$p\mathrm{H} = 7{\cdot}0 + 2{\cdot}37 - 2{\cdot}37 = 7{\cdot}0,$$

i.e., the solution is approximately neutral. On the other hand, for a dilute solution of ammonium formate :

$$p\mathrm{H} = 7{\cdot}0 + 1{\cdot}88 - 2{\cdot}37 = 6{\cdot}51,$$

(Formic acid : $K_a = 1{\cdot}77 \times 10^{-4}$; $pK_a = 3{\cdot}75$.)

i.e., the solution reacts slightly acid.

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* This applies only if the original assumptions as to activity coefficients are justified. In solutions of appreciable ionic strength, the activity coefficients of the ions will vary with the total ionic strength.

I, 20. Buffer solutions.—A solution of 0·0001N hydrochloric acid should have a pH equal to 4, but the solution is extremely sensitive to traces of alkali from the glass of the containing vessel and to ammonia from the air. Likewise a 0·0001N solution of sodium hydroxide, which should have a pH of 10, is sensitive to traces of carbon dioxide from the atmosphere. Aqueous solutions of potassium chloride and of ammonium acetate have a pH of about 7. The addition of 1 ml. of normal hydrochloric acid to 1 litre of the solution results in a change of pH to 3 in the former case and in very little change in the latter. The resistance of a solution to changes in hydrogen ion concentration upon the addition of small amounts of acid or alkali is termed **buffer action**; a solution which possesses such properties is known as a **buffer solution.** It is said to possess "reserve acidity" and "reserve alkalinity." Solutions of which the pH values (determined by reference to the hydrogen electrode) are known, which can be readily prepared, and which are unaffected by small additions of alkali or acid, are required for the colorimetric determination of hydrogen ion concentration (see Section **V, 6**) and for other purposes.

Buffer solutions usually consist of solutions containing a mixture of a weak acid or base and its salt. In order to understand buffer action, let us study first the equilibrium between a weak acid and its salt. The dissociation of a weak acid is given by:

$$HA \rightleftharpoons H^+ + A^-,$$

and its magnitude is controlled by the value of the dissociation constant K_a:

$$\frac{a_{H^+} \times a_{A^-}}{a_{HA}} = K_a, \text{ or } a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a \qquad \text{(i)},$$

where a_x refers to the activity of the species x. The expression may be approximated by writing concentrations for activities (strictly speaking, it will be recalled (Section **I, 5**), activity = concentration × activity coefficient):

$$[H^+] = \frac{[HA]}{[A^-]} \times K_a \qquad \text{(ii)}.$$

This equilibrium applies to a mixture of an acid HA and its salt, say, MA. If the concentration of the acid be c_a and that of the salt be c_s, then the concentration of the undissociated portion of the acid is $c_a - [H^+]$. The solution is electrically neutral, hence $[A^-] = c_s + [H^+]$ (the salt is completely dissociated). Substituting these values in the equilibrium equation (ii), we have:

$$[H^+] = \frac{c_a - [H^+]}{c_s + [H^+]} \times K_a \qquad \text{(iii)}.$$

This is a quadratic equation for $[H^+]$ and may be solved in the usual manner. It can, however, be simplified by introducing the following further approximations. In a mixture of a weak acid and its salt, the dissociation of the acid is repressed by the common ion effect, and $[H^+]$ may be taken as negligibly small by comparison with c_a and c_s. Equation (iii) then reduces to:

$$[H^+] = \frac{c_a}{c_s} \cdot K_a, \textit{ or } [H^+] = \frac{[\text{Acid}]}{[\text{Salt}]} \times K_a \qquad \text{(iv)},$$

or

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{(v)}.$$

Similarly for a mixture of a weak base of dissociation constant K_b and its salt with a strong acid:

$$[OH^-] = \frac{[\text{Base}]}{[\text{Salt}]} \times K_b \qquad \text{(vi)}$$

or

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad \text{(vii)}.$$

Let us confine our attention to the case in which the concentrations of the acid and its salt are equal, *i.e.*, of a half neutralised acid. Then $pH = pK_a$. Thus the pH of a half neutralised solution of a weak acid is equal to the negative logarithm of the dissociation constant of the acid. For acetic acid, $K_a = 1{\cdot}82 \times 10^{-5}$, $pK_a = 4{\cdot}74$; a half neutralised solution of, say, $0{\cdot}1N$ acetic acid will have a pH of $4{\cdot}74$. If we add a small concentration of H^+ ions to such a solution, the former will combine with the acetate ions to form undissociated acetic acid:

$$H^+ + C_2H_3O_2^- \rightleftharpoons H.C_2H_3O_2.$$

Similarly, if a small concentration of hydroxyl ions be added, the latter will combine with the hydrogen ions arising from the dissociation of the acetic acid and form unionised water; the equilibrium will be disturbed and more acetic acid will dissociate to replace the hydrogen ions removed in this way. In either case, the concentration of the acetic acid and acetate ion (or salt) will not be appreciably changed. It follows from equation (v) that the *p*H of the solution will not be materially affected.

The solution containing equal concentrations of acid and its salt, or a half neutralised solution of the acid, has the maximum buffer capacity. Other mixtures also possess considerable buffer capacity, but the *p*H will differ slightly from the half neutralised acid. Thus in a quarter neutralised solution of acid, [Acid] = 3 [Salt] :

$$\begin{aligned} pH &= pK_a + \log 1/3 \doteq pK_a + 1{\cdot}52, \\ &= pK_a - 0{\cdot}48. \end{aligned}$$

For a three-quarter neutralised acid, [Salt] = 3 [Acid] :

$$\begin{aligned} pH &= pK_a + \log 3, \\ &= pK_a + 0{\cdot}48. \end{aligned}$$

In general, we may state that the buffering capacity is maintained for mixtures within the range 1 acid : 10 salt and 10 acid : 1 salt. The approximate *p*H range of a weak acid buffer is :

$$pH = pK_a \pm 1.$$

The concentration of the acid is usually of the order 0·05 – 0·2 molar. Similar remarks apply to weak bases.

The preparation of a buffer solution of a definite *p*H is a simple process if the acid (or base) of appropriate dissociation constant is found : small variations in *p*H are obtained by variations in the ratio of the acid to the salt concentration. One example is given in Table VII,

TABLE VII. *p*H OF ACETIC ACID-SODIUM ACETATE BUFFER MIXTURES.*

10 ml. mixtures of x ml. of 0·2M acetic acid and y ml. of 0·2M sodium acetate.

Acetic Acid (x *ml.*)	*Sodium Acetate* (y *ml.*)	*p*H
9·5	0·5	3·42
9·0	1·0	3·72
8·0	2·0	4·05
7·0	3·0	4·27
6·0	4·0	4·45
5·0	5·0	4·63
4·0	6·0	4·80
3·0	7·0	4·99
2·0	8·0	5·23
1·0	9·0	5·57
0·5	9·5	5·89

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* See Appendix, Section **A, 10.**

Before leaving the subject of buffer solutions, it is necessary to draw attention to a possible erroneous deduction from equation (v), namely, that the hydrogen ion concentration of a buffer solution is dependent only upon the ratio of the concentrations of acid and salt and upon K_a, and not upon the actual concentrations; otherwise expressed, that the pH of such a buffer mixture should not change upon dilution with water. This is approximately although not strictly true. In deducing equation (ii), concentrations have been substituted for activities, a step which is not entirely justifiable except in dilute solutions. Theoretically, the expression controlling buffer action is:

$$a_{\mathrm{H}^+} = \frac{a_{\mathrm{HA}}}{a_{\mathrm{A}^-}} \times K_a = \frac{c_a \cdot f_a}{c_s \cdot f_{\mathrm{A}^-}} \times K_a \qquad \text{(viii)}$$

where a and f refer to activities and activity coefficients respectively of the species indicated in the subscript. The activity coefficient f_a of the undissociated acid is approximately unity in dilute aqueous solution. Expression (viii) thus becomes:

$$a_{\mathrm{H}^+} = \frac{[\mathrm{Acid}]}{[\mathrm{Salt}] \times f_{\mathrm{A}^-}} \times K_a \qquad \text{(ix)},$$

or

$$p\mathrm{H} = pK_a + \log [\mathrm{Salt}]/[\mathrm{Acid}] + \log f_{\mathrm{A}^-} \qquad \text{(x)}.$$

According to the Debye-Hückel-Onsager theory, the activity coefficient of an ion f_i in aqueous solution at 25°C is given by:

$$\log f_i = -\frac{0{\cdot}505 z_i^2 \mu^{0\cdot5}}{1 + A\mu^{0\cdot5}} + B\mu,$$

where z_i is the valency of the ion, μ is the ionic strength of the solution, and A and B are constants. This may be written in the form:

$$\log f_i = -0{\cdot}505\, z_i^2 \mu^{0\cdot5} + C\mu,$$

where C is another constant approximately equal to $0{\cdot}505\ z_i^2 A + B$ and usually has a value varying between 0·2 and 1·5. Substituting for f_{A^-} in (v), we obtain:

$$p\mathrm{H} = pK_a + \log [\mathrm{Salt}] / [\mathrm{Acid}] - 0{\cdot}505 z_i^2 \mu^{0\cdot5} + C\mu \qquad \text{(xi)}.$$

The activity coefficient of the ion f_{A^-} generally increases with decrease of concentration, so that when a buffer solution is diluted, f_{A^-} increases and consequently a_{H^+} will increase (equation (ix)). For most practical purposes the change is small, but for exact work the change must be taken into account. The addition of salts to buffer mixtures results in a change of the ionic strength of the solution ; this will affect the pH of the solution (equation (xi)). Indeed, in all buffer solutions a correction should, strictly speaking, be applied for the ionic strength of the solution.

Buffer mixtures are not confined to mixtures of monobasic acids or monoacid bases and their salts. We may employ a mixture of salts of a polybasic acid, *e.g.*, NaH_2PO_4 and Na_2HPO_4. The salt NaH_2PO_4 is completely dissociated :

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-.$$

The ion $H_2PO_4^-$ acts as a monobasic acid :

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--},$$

for which K ($\equiv K_2$ for phosphoric acid) is $6{\cdot}2 \times 10^{-8}$. The addition of the salt Na_2HPO_4 is analogous to the addition of, say, acetate ions to a solution of acetic acid, since the tertiary ionisation of phosphoric acid ($HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$) is small ($K_3 = 5 \times 10^{-13}$). The mixture of NaH_2PO_4 and Na_2HPO_4 is therefore an effective buffer over the range pH $7{\cdot}2 \pm 1{\cdot}0$ ($= pK \pm 1$).

Buffer solutions find many applications in quantitative analysis. Many precipitations are made in certain ranges of pH values. Examples are given in Section **I, 61** under Separations ; many others will be found scattered throughout the text. Buffer solutions are also employed in the colorimetric determination of pH with the aid of indicators (Section **V, 6**).

VOLUMETRIC ANALYSIS

In the foregoing pages we have studied some general theory, a knowledge of which is indispensable for the comprehension of the processes of quantitative analysis, both gravimetric and volumetric. We will now confine our attention to the principles of volumetric analysis and postpone the parallel study of gravimetric analysis to a later stage (Section **I, 54**).

I, 21. Volumetric analysis, or quantitative chemical analysis by measure, consists essentially in determining the volume of a solution of accurately known concentration which is required to react quantitatively with the solution of the substance being determined. The solution of accurately known strength is called the **standard solution** ; it contains a definite number of gram equivalents (see Section **I, 23**) per litre. The weight of the substance to be determined is then calculated from the volume of the standard solution and the known laws of chemical equivalence.

The standard solution is usually added from a graduated vessel, called a **burette.** The process of adding the standard solution until the reaction is just complete is termed a **titration,** and the substance to be determined is **titrated.** The point at which this occurs is called the **equivalence point** or the **theoretical** (*or* **stoichiometric**) **end point.** The completion of the titration should, as a rule, be detectable by some change unmistakable to the eye produced by the standard solution itself (*e.g.*, potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an **indicator.** After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a colour change or the formation of a turbidity) in the liquid being titrated. The point at which this occurs is called the **end point of the titration.** In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs ; this represents the **titration error.** We should always endeavour to select an indicator and also the experimental conditions such that the difference between the visible end point and the equivalence point is as small as possible.

For use in volumetric analysis a reaction must fulfil the following conditions :

1. There must be a simple reaction which can be expressed by a chemical equation ; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.

2. The reaction should be practically instantaneous or proceed with very great speed. (Most ionic reactions satisfy this condition.) In some cases the addition of a *catalyst* increases the speed of a reaction.

3. There must be a marked change in some physical or chemical property of the solution at the equivalence point.

4. An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction. [If no visible indicator is available for the detection of the equivalence point, the latter can often be determined by following during the course of the titration (*a*) the change of the potential of a suitable electrode (**potentiometric titration,** see Sections **I, 53**), or (*b*) the change of the electrical conductance of the solution (**conductometric titration**).]

Volumetric methods are, as a rule, susceptible of high accuracy (1 part in 1000) and possess several advantages, wherever applicable, over gravimetric methods. They need simpler apparatus, tedious and difficult separations can often be avoided, and are, generally, quickly performed. The following are required for volumetric analysis : (i) Calibrated measuring vessels including burettes, pipettes and measuring flasks (see Sections **II, 20-22**). (ii) Substances of known purity for the preparation of standard solutions. (iii) An indicator or other device (see Section **I, 53**) for detecting the completeness of the reaction.

I, 22. Classification of reactions in volumetric analysis.— The reactions employed in volumetric analysis fall into two main classes :

(*a*) Those in which no change in valency occurs ; these are dependent upon the combination of ions.

(*b*) Oxidation-reduction reactions ; these involve a change of valency or, otherwise expressed, a transfer of electrons.

For purposes of convenience, however, these two types of reactions are divided into three main classes :

1. Neutralisation reactions, or acidimetry and alkalimetry. These include the titration of free bases or those formed from salts of weak acids by hydrolysis with a standard acid (**acidimetry**), and the titration of free acids or those formed by the hydrolysis of salts of weak bases with a standard base (**alkalimetry**). These reactions involve the combination of hydrogen and hydroxyl ions to form water.

2. Precipitation reactions. These depend upon the combination of ions, other than hydrogen and hydroxyl ions, to form either a simple precipitate, as in the titration of silver with a solution of a chloride (Section **III, 24**), or a complex ion, as in the titration of a cyanide with silver nitrate solution (Section **III, 41** ; $2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$).

3. Oxidation-reduction reactions. Under this heading are included all reactions involving change in oxidation number (Section **I, 23**) or transfer of electrons (Section **I, 23**) *among the* reacting substances. The standard solutions are either oxidising or reducing agents. The principal oxidising agents are potassium permanganate, potassium dichromate, ceric sulphate, manganic sulphate, iodine, potassium iodate, potassium bromate and chloramine-T. Frequently used reducing agents are ferrous and stannous compounds, sodium thiosulphate, arsenious oxide and titanous chloride or sulphate.

I, 23. Equivalent weights. Normal solutions.—A **standard solution** is one which contains a known weight of the reagent in a definite volume of the solution. A **molar solution** is one which contains one gram molecular weight of the reagent per litre of solution. A **normal solution** of a reagent is one that contains one gram equivalent weight* per litre of solution. It is designated by *N*. Semi-normal, penti-normal, decinormal and centi-normal solutions are often required ; these are shortly written $N/2$ or $0{\cdot}5N$, $N/5$ or $0{\cdot}2N$, $N/10$ or $0{\cdot}1N$, and $N/100$ or $0{\cdot}01N$ respectively.

The above definition of normal solution utilises the term " equivalent weight." This quantity varies with the type of reaction, and, since it is difficult to give a clear definition of " equivalent weight " which will cover all reactions, it is proposed to discuss this subject in some detail below. It often happens that the same compound possesses different equivalent weights in different chemical reactions. The situation may therefore arise in which a solution may have normal concentration when employed for one purpose, and a different normal concentration when used in another chemical reaction.

Neutralisation reactions.—The **equivalent weight of an acid** is that weight of it which contains one replaceable hydrogen,

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* Sometimes also called equivalent, gram equivalent or equivalent weight.

i.e., 1·008 (more accurately 1·0078) grams of hydrogen. The equivalent weight of a monobasic acid, such as hydrochloric, hydrobromic, hydriodic, nitric, perchloric or acetic acid, is identical with its molecular weight. A normal solution of a monobasic acid will therefore contain one gram molecular weight (or 1 mol) in a litre of solution. The equivalent weight of a dibasic acid (*e.g.*, sulphuric or oxalic acid), or of a tribasic acid (*e.g.*, phosphoric acid) is likewise 1/2 and 1/3 respectively of its molecular weight.

The **equivalent weight of a base** is that weight of it which contains one replaceable hydroxyl group, *i.e.*, 17·008 grams of ionisable hydroxyl. 17·008 grams of hydroxyl are equivalent to 1·008 grams of hydrogen. The equivalent weights of sodium hydroxide, potassium hydroxide and ammonium hydroxide are 1 mol, of calcium hydroxide, strontium hydroxide and barium hydroxide 1/2 mol.

Salts of strong bases and weak acids possess alkaline reactions in aqueous solution because of hydrolysis (Section **I, 18**). Sodium carbonate, with methyl orange as indicator, reacts with two mols of hydrochloric acid to form two mols of sodium chloride; hence its equivalent weight is 1/2 mol. Borax, under similar conditions, also reacts with two mols of hydrochloric acid, and its equivalent weight is, likewise, 1/2 mol.

Precipitation reactions.—Here the equivalent weight is the weight of the substance which contains or reacts with one gram atom of a univalent metal (which is equivalent to 1·008 grams of hydrogen), 1/2 gram atom of a bivalent metal, etc. For a metal, the equivalent weight is the atomic weight divided by the valency. For a reagent which reacts with this metal, the equivalent weight is the weight of it which reacts with one equivalent of the metal. The reactive constituents of a salt are its ions. The **equivalent weight of a salt** in a precipitation reaction is the gram molecular weight of the salt divided by the total valency of the *reacting* ion. Thus the equivalent weight of silver nitrate in the titration of chloride is its molecular weight.

In a complex formation reaction, the equivalent weight is most simply deduced by writing down the ionic equation of the reaction. For example, the equivalent weight of potassium cyanide in the titration with silver ions is two mols, since the reaction is:

$$2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-.$$

Oxidation-reduction reactions.—The equivalent weight of an oxidising or reducing agent is most simply defined as that weight of the reagent which reacts with or contains 1·008 grams of available hydrogen or 8·000 grams of available oxygen. By " available " is meant capable of being utilised in oxidation or reduction. The amount of available oxygen may be indicated by writing the *hypothetical* equation, *e.g.*,

$$2KMnO_4 = K_2O + 2MnO + 5O,$$

i.e., in acid solution $2KMnO_4$ gives up 5 atoms of available oxygen which is taken up by the reducing agent, hence its equivalent weight is $2KMnO_4/10$. For potassium dichromate in acid solution, the hypothetical equation is:

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O.$$

The equivalent weight is $K_2Cr_2O_7/6$. This elementary treatment is limited in application, but is useful for beginners.

A more general view is obtained by a consideration of (*a*) the number of electrons involved in the partial ionic equation representing the reaction, and (*b*) the change in the " oxidation number " of a significent element in the oxidant or reductant. Both methods will be considered in some detail.

In quantitative analysis we are chiefly concerned with reactions which take place in solution, *i.e.*, ionic reactions. We shall therefore limit our discussion of oxidation-reduction to such reactions. The oxidation of ferrous chloride by chlorine in aqueous solution may be written:

$$2FeCl_2 + Cl_2 = 2FeCl_3,$$

or may be expressed ionically:

$$2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-.$$

The ferrous ion Fe^{++} is converted into the ferric ion Fe^{+++} (oxidation), and the neutral chlorine molecule into negatively charged chloride ions Cl^- (reduction). According to the electronic conception of the constitution of matter, the conversion of Fe^{++} into Fe^{+++} requires the loss of one electron, and the transformation of the neutral chlorine molecule into chloride ions necessitates the gain of two electrons. This leads to the view that, for reactions in solution, oxidation is a process involving a loss of electrons, as in

$$Fe^{++} - \epsilon = Fe^{+++},$$

and reduction is the process resulting in a gain of electrons, as in

$$Cl_2 + 2\epsilon = 2Cl^-.$$

In the actual oxidation-reduction process electrons are transferred from the reducing agent to the oxidising agent. This leads to the following definitions. **Oxidation** is the process which results in the loss of one or more electrons by atoms or ions. **Reduction** is the process which results in the gain of one or more electrons by atoms or ions. An **oxidising agent** is one that gains electrons and is reduced to a lower valency condition. A **reducing agent** is one that loses electrons and is oxidised to a higher valency condition.

The following are examples of oxidising agents which are of importance in quantitative analysis: potassium permanganate, potassium dichromate, ceric sulphate, manganic sulphate, iodine, potassium bromate, potassium iodate and chloramine-T. Examples of reducing agents are: ferrous sulphate, metallic iron, sodium thiosulphate, sodium arsenite or arsenious oxide, oxalic acid, titanous chloride or sulphate and chromous sulphate.

In all oxidation-reduction processes (or **redox** processes) there will be a reactant undergoing oxidation and one undergoing reduction, since the two reactions are complementary to one another and occur simultaneously—one cannot take place without the other. The reagent suffering oxidation is termed the reducing agent or **reductant,** and the reagent undergoing reduction is called the oxidising agent or **oxidant.** The study of the electron changes in the oxidant and reductant forms the basis of the **ion-electron method** for balancing ionic equations, a method developed in some detail by Jette and La Mer in 1927. The equation is accordingly first divided into two balanced, partial equations representing the oxidation and reduction respectively. It must be remembered that the reactions take place in aqueous solution so that in addition to the ions supplied by the oxidant and reductant, the molecule of water H_2O, hydrogen ions H^+ and hydroxyl ions OH^- are also present, and may be utilised in balancing the partial ionic equation. The unit change in oxidation or reduction is a charge of one electron, which will be denoted by ϵ. To appreciate the principles involved, let us consider first the reaction between ferric chloride and stannous chloride in aqueous solution. The partial ionic equation for the reduction is:

$$Fe^{+++} \rightarrow Fe^{++} \qquad (a),$$

and for the oxidation is:

$$Sn^{++} \rightarrow Sn^{++++} \qquad (b).$$

The equations must be balanced not only with regard to the number and kind of atoms, but also electrically, that is, the net electric charge on each side must be the same. Equation (*a*) can be balanced by adding one electron to the left hand side :

$$\mathrm{Fe^{+++}} + \epsilon \rightleftharpoons \mathrm{Fe^{++}} \qquad (a'),$$

and equation (*b*) by adding two electrons to the right hand side :

$$\mathrm{Sn^{++}} \rightleftharpoons \mathrm{Sn^{++++}} + 2\epsilon \qquad (b').$$

These partial equations must then be multiplied by coefficients which result in the number of electrons utilised in one reaction being equal to those liberated in the other. Thus equation (*a′*) must be multiplied by two, and we have :

$$2\mathrm{Fe^{+++}} + 2\epsilon \rightleftharpoons 2\mathrm{Fe^{++}} \qquad (a'');$$

$$\mathrm{Sn^{++}} \rightleftharpoons \mathrm{Sn^{++++}} + 2\epsilon \qquad (b'').$$

Adding (*a″*) and (*b″*), we obtain :

$$2\mathrm{Fe^{+++}} + \mathrm{Sn^{++}} + 2\epsilon \rightleftharpoons 2\mathrm{Fe^{++}} + \mathrm{Sn^{++++}} + 2\epsilon,$$

and by cancelling the electrons common to both sides, the simple ionic equation is obtained :

$$2\mathrm{Fe^{+++}} + \mathrm{Sn^{++}} = 2\mathrm{Fe^{++}} + \mathrm{Sn^{++++}}.$$

The following facts must be borne in mind. All strong electrolytes are completely dissociated ; hence only the ions actually taking part or resulting from the reaction need appear in the equation. Substances which are only slightly ionised, such as water, or which are sparingly soluble and thus yield only a small concentration of ions, *e.g.*, silver chloride and barium sulphate, are, in general, written in the molecular form because most of the substance is present in this state.

The complete rules for the application of the ion-electron method may be expressed as follows :—

(1) Ascertain the products of the reaction.

(2) Set up a partial equation for the oxidising agent.

(3) Set up a partial equation for the reducing agent in the same way.

(4) Multiply each partial equation by a factor so that when the two are added the electrons just compensate each other.

(5) Add the partial equations and cancel out substances which appear on both sides of the equation.

A few examples follow.

Reaction I : the reduction of potassium permanganate in the presence of dilute sulphuric acid.

The first partial equation (reduction) is :

$$MnO_4^- \rightarrow Mn^{++}.$$

To balance atomically, $8H^+$ is required :

$$MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O\ ;$$

and to balance it electrically 5 ϵ is needed on the left hand side:

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O.$$

The second partial equation (oxidation) is :

$$Fe^{++} \rightarrow Fe^{+++}.$$

To balance this electrically one electron must be added to the right hand side or subtracted from the left hand side :

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon.$$

Now the gain and loss of electrons must be equal. One permanganate ion utilises 5 electrons, and one ferrous ion liberates 1 electron ; hence the two partial equations must take place in the ratio of 1 : 5.

$$\begin{array}{l} MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O \\ \qquad\qquad 5(Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon) \\ \hline \textit{or}\ MnO_4^- + 8H^+ + 5Fe^{++} = Mn^{++} + 5Fe^{+++} + 4H_2O. \end{array}$$

Reaction II : the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.

$$Cr_2O_7^{--} \rightarrow Cr^{+++}\ ;$$

$$Cr_2O_7^{--} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O.$$

To balance electrically, add 6ϵ to the left hand side :

$$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O.$$

The various stages in the deduction of the second partial equation are :

$$I^- \rightarrow I_2\ ;$$

$$2I^- \rightarrow I_2\ ;$$

$$2I^- \rightleftharpoons I_2 + 2\epsilon.$$

One dichromate ion uses 6ϵ, and two iodide ions liberate 2ϵ ; hence the two partial equations take place in the ratio of 1 : 3.

$$\begin{array}{l} Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O \\ \qquad\qquad 3(2I^- \rightleftharpoons I_2 + 2\epsilon) \\ \hline \textit{or}\ Cr_2O_7^{--} + 14H^+ + 6I^- = 2Cr^{+++} + 7H_2O + 3I_2. \end{array}$$

We can now apply our knowledge of partial ionic equations to the subject of equivalents. The standard oxidation-reduction process is $H \rightleftharpoons H^+ + \epsilon$, where ϵ represents an electron per atom or one Faraday (96,500 coulombs) per gram atom. If we know the change in the number of electrons per ion in any oxidation-reduction reaction, the equivalent may be calculated. The **equivalent weight of an oxidant or reductant** is the molecular weight divided by the number of electrons which one molecule of the substance gains or loses in the reaction.

We will write down the partial equations for four typical reactions :

$$\begin{array}{ll} MnO_4^{-} + 8H^{+} + 5\epsilon = Mn^{++} + 4H_2O. & \text{Eq. wt.} = MnO_4^{-}/5 = KMnO_4/5. \\ Cr_2O_7^{--} + 14H^{+} + 6\epsilon = 2Cr^{+++} + 7H_2O. & \text{Eq. wt.} = Cr_2O_7^{--}/6 = K_2Cr_2O_7/6. \\ Fe^{++} - \epsilon = Fe^{+++} & \text{Eq. wt.} = Fe^{++}/1 = FeSO_4/1. \\ C_2O_4^{--} - 2\epsilon = 2CO_2. & \text{Eq. wt.} = C_2O_7^{--}/2 = H_2C_2O_4/2. \end{array}$$

For convenience of reference the partial ionic equation for a number of oxidising and reducing agents are collected in Table VIII.

The other procedure which is of value in the calculation of the equivalent weights of substance is the "**oxidant number**" **method.** The student should be thoroughly conversant with the significance of " oxidation number " and its use in balancing oxidation-reduction equations.* The **equivalent weight of an oxidising agent** is determined by the change in oxidation number which the reduced element experiences. It is that quantity of oxidant which involves a change of one unit in the oxidation number. Thus in the normal reduction of potassium permanganate in the presence of dilute sulphuric acid to a manganous salt :

$$\overset{+1}{K}\,\overset{+7}{Mn}\,\overset{-8}{O_4} \rightarrow \overset{+2}{Mn}\,\overset{+6}{S}\,\overset{-8}{O_4}$$

the change in the oxidation number of the manganese is from +7 to +2.

The equivalent weight of potassium permanganate is therefore 1/5 mol or by 5 units of reduction. Similarly for the reduction of potassium dichromate in acid solution :

$$\overset{+2}{K_2}\,\overset{+12}{Cr_2}\,\overset{-14}{O_7} \rightarrow \overset{+6}{Cr_2}\overset{-6}{(SO_4)_3}$$

the change in oxidation number of *two* atoms of chromium is from +12 to +6, or by 6 units of reduction. The equivalent weight of potassium dichromate is accordingly 1/6 mol. In order to find the equivalent weight of an oxidising agent, we divide the molecular weight by the change in oxidation number *per molecule* which some key element in the substance undergoes.

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* A detailed account will be found in the author's *Text Book of Qualitative Chemical Analysis*, 1937, p. 42 *et seq.* (Longmans, Green and Co.)

TABLE VIII. IONIC EQUATIONS FOR USE IN THE CALCULATION OF THE EQUIVALENT WEIGHTS OF OXIDISING AND REDUCING AGENTS.

Substance.	*Partial Ionic Equation.*
	OXIDANTS
Potassium permanganate (acid)	$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O$
Potassium permanganate (neutral)	$MnO_4^- + 2H_2O + 3\epsilon \rightleftharpoons MnO_2 + 4OH^-$
Potassium permanganate (strongly alkaline)	$MnO_4^- + \epsilon \rightleftharpoons MnO_4^{--}$
Ceric sulphate	$Ce^{++++} + \epsilon \rightleftharpoons Ce^{+++}$
Potassium dichromate	$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O$
Chlorine	$Cl_2 + 2\epsilon \rightleftharpoons 2Cl^-$
Bromine	$Br_2 + 2\epsilon \rightleftharpoons 2Br^-$
Iodine	$I_2 + 2\epsilon \rightleftharpoons 2I^-$
Ferric chloride	$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$
Potassium bromate	$BrO_3^- + 6H^+ + 6\epsilon \rightleftharpoons Br^- + 3H_2O$
Potassium iodate	$IO_3^- + 6H^+ + 6\epsilon \rightleftharpoons I^- + 3H_2O$
Sodium hypochlorite	$ClO^- + H_2O + 2\epsilon \rightleftharpoons Cl^- + 2OH^-$
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2\epsilon \rightleftharpoons 2H_2O$
Manganese dioxide	$MnO_2 + 4H^+ + 2\epsilon \rightleftharpoons Mn^{++} + 2H_2O$
Sodium bismuthate	$BiO_3^- + 6H^+ + 2\epsilon \rightleftharpoons Bi^{+++} + 3H_2O$
Nitric acid (conc.)	$NO_3^- + 2H^+ + \epsilon \rightleftharpoons NO_2 + H_2O$
Nitric acid (dilute)	$NO_3^- + 4H^+ + 3\epsilon \rightleftharpoons NO + 2H_2O$
	REDUCTANTS
Hydrogen	$H_2 - 2\epsilon \rightleftharpoons 2H^+$
Zinc	$Zn - 2\epsilon \rightleftharpoons Zn^{++}$
Hydrogen sulphide	$H_2S - 2\epsilon \rightleftharpoons 2H^+ + S$
Hydrogen iodide	$2HI - 2\epsilon \rightleftharpoons I_2 + 2H^+$
Oxalic acid	$C_2O_4^{--} - 2\epsilon \rightleftharpoons 2CO_2$
Ferrous sulphate	$Fe^{++} - \epsilon \rightleftharpoons Fe^{+++}$
Sulphurous acid	$H_2SO_3 + H_2O - 2\epsilon \rightleftharpoons SO_4^{--} + 4H^+$
Sodium thiosulphate	$2S_2O_3^{--} - 2\epsilon \rightleftharpoons S_4O_6^{--}$
Titanous sulphate	$Ti^{+++} - \epsilon \rightleftharpoons Ti^{++++}$
Stannous chloride	$Sn^{++} - 2\epsilon \rightleftharpoons Sn^{++++}$
Stannous chloride (in presence of hydrochloric acid)	$Sn^{++} + 6Cl^- - 2\epsilon \rightleftharpoons SnCl_6^{--}$
Hydrogen peroxide	$H_2O_2 - 2\epsilon \rightleftharpoons 2H^+ + O_2$

The **equivalent weight of a reducing agent** is similarly determined by the change in oxidation number which the oxidised element suffers. Consider the conversion of ferrous into ferric sulphate :

$$\overset{+2\ -2}{2(FeSO_4)} \rightarrow \overset{+6\ -6}{Fe_2(SO_4)_3}.$$

Here the change in oxidation number *per atom* of iron is from +2 to +3, or by 1 unit of oxidation, hence the equivalent weight of ferrous sulphate is 1 mol. Another important reaction is the oxidation of oxalic acid to carbon dioxide and water :

$$\overset{-2}{H_2}\,\overset{+6}{C_2}\,\overset{-8}{O_4} \rightarrow 2\overset{+4}{C}\,\overset{-4}{O_2}$$

The change in oxidation number of two atoms of carbon is from +6 to +8, or by 2 units of oxidation. The equivalent weight of oxalic acid is therefore 1/2 mol.

In general, it may be stated :

(i) The equivalent weight of an element taking part in an oxidation-reduction (redox) reaction is the atomic weight divided by the change in oxidation number.

(ii) When an atom in any complex molecule suffers a change in oxidation number (oxidation or reduction), the equivalent weight of the substance is the molecular weight divided by the change in oxidation number of the oxidised or reduced element. If more than one atom of the reactive element is present, the molecular weight is divided by the total change in oxidation number.

A useful summary of the common oxidising and reducing agents, together with the various transformations which they undergo, is given in Table IX.

We are now in a position to understand more clearly why the equivalent weights of some substances vary with the reaction. We will consider two familiar examples by way of illustration. A normal solution of ferrous sulphate $FeSO_4$, $7H_2O$ will have an equivalent weight of 1 mol when employed as a reductant, and 1/2 mol when employed as a precipitant. A solution of ferrous sulphate which is normal as a precipitant will be half normal as a reductant. Potassium tetroxalate $KHC_2O_4,H_2C_2O_4,2H_2O$ contains three replaceable hydrogen atoms ; its equivalent weight in neutralisation reactions is therefore 1/3 mol :

$$KHC_2O_4,H_2C_2O_4,2H_2O + 3KOH = 2K_2C_2O_4 + 5H_2O.$$

As a reducing agent, a gram molecular weight contains $2C_2O_4^{--}$, and the equivalent weight is accordingly 1/4 mol :

$$C_2O_4^{--} - 2\epsilon = 2CO_2.$$

A solution of the salt which is 3*N* as an acid is 4*N* as a reducing agent.

I, 24. Advantages of the use of the equivalent system for the preparation of standard solutions.—The most important advantage of the equivalent system is that the calculations of volumetric analysis are rendered very simple, since at the

TABLE IX

Substance	*Radical or element involved*	*O.N. of "effective" element*	*Reduction product*	*New O.N.*	*Decrease in O.N.*	*Gain in in electrons*
COMMON OXIDISING AGENTS						
$KMnO_4$ (acid)	MnO_4^-	$+7$	Mn^{++}	$+2$	5	5
$KMnO_4$ (neutral)	MnO_4^-	$+7$	MnO_2 or Mn^{++++})	$+4$	3	3
$KMnO_4$ (strongly alkaline)	MnO_4^-	$+7$	MnO_4^{--}	$+6$	1	1
$K_2Cr_2O_7$	$Cr_2O_7^{--}$	$+6$	Cr^{+++}	$+3$	3	3
HNO_3 (dil.)	NO_3^-	$+5$	NO	$+2$	3	3
HNO_3 (conc.)	NO_3^-	$+5$	NO_2	$+4$	1	1
Cl_2	Cl	0	Cl^-	-1	1	1
Br_2	Br	0	Br^-	-1	1	1
I_2	I	0	I^-	-1	1	1
$3HCl : 1HNO_3$	Cl	0	Cl^-	-1	1	1
H_2O_2	O	0	O^{--}	-2	2	2
Na_2O_2	O	0	O^{--}	-2	2	2
$KClO_3$	ClO_3^-	$+5$	Cl^-	-1	6	6
$KBrO_3$	BrO_3^-	$+5$	Br^-	-1	6	6
KIO_3	IO_3^-	$+5$	I^-	-1	6	6
$NaOCl$	OCl^-	$+1$	Cl^-	-1	2	2
$FeCl_3$	Fe^{+++}	$+3$	Fe^{++}	$+2$	1	1
$Ce(SO_4)_2$	Ce^{++++}	$+4$	Ce^{+++}	$+3$	1	1
COMMON REDUCING AGENTS						
H_2SO_3 or Na_2SO_3	SO_3^{--}	$+4$	SO_4^{--}	$+6$	2	2
H_2S	S^{--}	-2	S°	0	2	2
HI	I^-	-1	I°	0	1	1
$SnCl_2$	Sn^{++}	$+2$	Sn^{++++}	$+4$	2	2
Metals, *e.g.*, Zn	Zn	0	Zn^{++}	$+2$	2	2
Hydrogen	H	0	H^+	$+1$	1	1
$FeSO_4$ (or any ferrous salt)	Fe^{++}	$+2$	Fe^{+++}	$+3$	1	1
Na_3AsO_3	AsO_3^{---}	$+3$	AsO_4^{---}	$+5$	2	2
$H_2C_2O_4$	$C_2O_4^{--}$	$+3$	C_2O	$+4$	1	1
$Ti_2(SO_4)_3$	Ti^{+++}	$+3$	Ti^{++++}	$+4$	1	1

end point the number of equivalents of the substance titrated is equal to the number of equivalents of the standard solution employed. We may write :

$$\text{Normality} = \frac{\text{Number of gram equivalents}}{\text{Number of litres}}$$

$$= \frac{\text{Number of milligram equivalents}}{\text{Number of millilitres (ml.)}^*}$$

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* See Section II, 17.

Hence: number of mg. equivalents = number of ml. × normality. If the volumes of solutions of two different substances A and B which exactly react with one another are V_A ml. and V_B ml. respectively, then these volumes severally contain the same number of gram equivalents or mg. equivalents of A and B. Thus:

$$V_A \times \text{normality}_A = V_B \times \text{normality}_B \qquad \text{(i)}.$$

In practice V_A, V_B and normality$_A$ (the standard solution) are known, hence normality$_B$ (the unknown solution) can be readily calculated.

Example 12. How many ml. of 0·2N hydrochloric acid are required to neutralise 25·0 ml. of 0·1N sodium hydroxide?

Substituting in equation (i), we obtain:

$$x \times 0{\cdot}2 = 25{\cdot}0 \times 0{\cdot}1, \text{ whence } x = \textit{12·5 ml.}$$

Example 13. How many ml. of N hydrochloric acid are required to precipitate completely 1 gram of silver nitrate?

The equivalent weight of $AgNO_3$ in a precipitation reaction is 1 mol or 169·89 g.

Hence 1 g. of $AgNO_3$ = 1 × 1000/169·89 = 5·886 mg. equivalents.

Now number of mg. equivalents of HCl = number of mg. equivalents of $AgNO_3$,

$$x \times 1 = 5{\cdot}886, \text{ whence } x = \textit{5·90 ml.}$$

Example 14. 25 Ml. of a ferrous sulphate solution react completely with 30 ml. of 0·125N potassium permanganate. Calculate the strength of the ferrous sulphate solution in grams $FeSO_4$ per litre.

A normal solution of $FeSO_4$ as a reductant contains 1 mol per litre or 151·90 g. per litre (Table IX). Let the normality of the ferrous sulphate solution be n_A. Then:

$$25 \times n_A = 30 \times 0{\cdot}125,$$

or

$$n_A = 30 \times 0{\cdot}125/25 = 0{\cdot}15N.$$

Hence the solution will contain 0·15 × 151·90 = *22·785 g. $FeSO_4$ per litre.*

Example 15. What volume of 0·127N reagent is required for the preparation of 1000 ml. of 0·1N solution?

$$V_A \times \text{normality}_A = V_B \times \text{normality}_B;$$

$$V_A \times 0{\cdot}127 = 1000 \times 0{\cdot}1;$$

or

$$V_A = 1000 \times 0{\cdot}1/0{\cdot}127 = \textit{787·4 ml.}$$

Hence it is necessary to dilute 787·4 ml. of 0·127N solution to 1 litre. Strictly speaking it is not correct to add 212·6 ml. of water, because there is usually a volume change on mixing. This change is so small, however, that diluted solutions are often prepared by the addition of the calculated amount of water to a measured volume of standard reagent.

I, 25. Preparation of standard solutions.—If a reagent is available in the pure state, a solution of definite normality is prepared simply by weighing out an equivalent weight, or a definite fraction or multiple thereof, dissolving it in the solvent, usually water, and making up the solution to a known volume. It is not really essential to weigh out the equivalent weight (or a multiple or sub-multiple thereof). In practice it is often more convenient to prepare the solution a *little* more concentrated than is ultimately required, and then to dilute it with distilled water until the desired normality is obtained. If N_1 is the required normality, V_1 the volume after dilution, N_2 the normality originally obtained and V_2 the original volume taken, $N_1V_1 = N_2V_2$, or $V_1 = N_2V_2/N_1$. The volume of water to be added to the volume V_2 is $(V_1 - V_2)$ ml. (compare *Example 15* in Section **I, 24**). The following is a list of some of the substances which can be obtained in a state of high purity and are therefore suitable for the preparation of standard solutions: sodium carbonate, potassium hydrogen phthalate, benzoic acid, borax, furoic acid, adipic acid, sulphamic acid, potassium bi-iodate, sodium oxalate, silver nitrate, sodium chloride, potassium chloride, iodine, potassium bromate, potassium iodate, potassium dichromate and arsenious oxide.

When the reagent is not available in the pure form as in the cases of most alkali hydroxides, some inorganic acids and various deliquescent substances, solutions of the approximate normality required are first prepared. These are then standardised by titration against a solution of a pure substance of known normality. It is generally best to standardise a solution by a reaction of the same type as that for which the solution is to be employed, and as nearly as possible under identical experimental conditions. The titration error and other errors are thus considerably reduced or are made to cancel out. This indirect method is employed for the preparation of solutions of *inter alia* most acids (for hydrochloric acid, the constant boiling point mixture of definite composition can be weighed out directly, if desired), sodium, potassium and barium hydroxides, potassium permanganate, ammonium and potassium thiocyanates, and sodium thiosulphate.

I, 26. Primary standard substances.—A primary standard substance should satisfy the following requirements:

1. It must be easy to obtain, to purify, to dry (preferably at

110°-120°C), and to preserve in a pure state. (This requirement is not usually met by hydrated substances since it is difficult to remove surface moisture completely without effecting partial decomposition.)

2. It should not be hygroscopic, but should be unalterable in ordinary air during weighing.

3. The substance should be capable of being tested for impurities by qualitative tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0·01-0·02 per cent.)

4. It should have a high equivalent weight so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0·1-0·2 mg. ; for an accuracy of 1 part in 1,000, it is necessary to employ samples weighing at least *ca.* 0·2 g.)

5. The substance should be readily soluble under the conditions in which it is employed.

6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are : Acidimetry and alkalimetry—sodium carbonate Na_2CO_3, borax $Na_2B_4O_7$, potassium hydrogen phthalate $KH.C_8H_4O_4$, constant boiling point hydrochloric acid, potassium bi-iodate $KH(IO_3)_2$, sulphamic acid NH_2SO_2OH, succinic acid $H_2.C_4H_4O_4$, benzoic acid $H.C_7H_5O_2$, furoic acid $H.C_5H_3O_2$, and adipic acid $H_2.C_6H_8O_4$.

Precipitation reactions—silver, silver nitrate, sodium chloride, and potassium chloride.

Oxidation-reduction reactions—potassium dichromate $K_2Cr_2O_7$, potassium bromate $KBrO_3$, potassium iodate KIO_3, potassium bi-iodate $KH(IO_3)_2$, iodine I_2, sodium oxalate $Na_2C_2O_4$, arsenious oxide As_2O_3, and electrolytic, or otherwise pure, iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as borax $Na_2B_4O_7,10H_2O$, oxalic acid $H_2C_2O_4,2H_2O$ and copper sulphate $CuSO_4,5H_2O$, are found by experiment to be satisfactory secondary standards.

THEORY OF ACIDIMETRY AND ALKALIMETRY

I, 27. Neutralisation indicators.—The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the **equivalence point, stoichiometrical point,** or **theoretical end point,** and corresponds to an aqueous solution of the acid and the base. If both the acid and base are strong electrolytes, the resultant solution will be neutral and have a *p*H of 7 (Section **I, 17**). But if either the acid or the base is a weak electrolyte, the salt will be hydrolysed to a certain degree and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact *p*H of the solution at the equivalence point can readily be calculated from the ionisation constant of the weak acid or the weak base and the concentration of the solution (see Section **I, 19**). For any actual titration the correct end point will be characterised by a definite value of the hydrogen ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances are available, called **neutralisation** or **acid-base indicators,** which possess different colours according to the hydrogen ion concentration of the solution. The chief characteristic of these indicators is that the change from a predominantly " acid " colour to a predominantly " alkaline " colour is not sudden and abrupt, but takes place within a small interval of *p*H (usually about two *p*H units) termed the **colour change interval** of the indicator. The position of the colour change interval in the *p*H scale varies widely with different indicators. For most acid-base titrations, we can therefore select an indicator which exhibits a distinct colour at a *p*H close to that obtaining at the equivalence point.

The first useful theory of indicator action was suggested by W. Ostwald. All indicators in general use are very weak organic acids or bases. Ostwald (1891) considered that the undissociated indicator acid (HIn) or base (InOH) had a different colour from that of its ion. The equilibria in aqueous solution may be written :

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-} \quad . \quad (ia),$$

and

$$\underset{\text{unionised colour}}{\mathrm{InOH}} \rightleftharpoons \mathrm{OH^-} + \underset{\text{ionised colour}}{\mathrm{In^+}} \quad (ib).$$

If the indicator is an anhydro-base (In), e.g., a free amine or substituted amine, the equilibrium is:

$$\mathrm{In} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH^-} + \mathrm{HIn^+} \qquad (ic).$$

Let us consider an acid indicator. In acid solution, *i.e.*, in the presence of excess of H^+ ions, the ionisation will be depressed (common ion effect) and the concentration of In^- will be very small; the colour will therefore be that of the unionised form. If the medium is alkaline, the decrease of $[H^+]$ will result in the further ionisation of the indicator. $[In^-]$ increases and the colour of the ionised form becomes apparent. By applying the law of mass action, we obtain:

$$\frac{a_{H^+} \times a_{In^-}}{a_{HIn}} = \frac{[H^+] \times [In^-]}{[HIn]} \times \frac{f_{H^+} \cdot f_{In^-}}{f_{HIn}} = K_{ina} \qquad (ii),$$

and
$$[H^+] = \frac{[HIn]}{[In^-]} \times K_{ina} \times \frac{f_{HIn}}{f_{H^+} \cdot f_{In^-}}$$

$$= \frac{[\text{Unionised form}]}{[\text{Ionised form}]} \times K_{Ina} \times \frac{f_{HIn}}{f_{H^+} \cdot f_{In^-}} \qquad (iii),$$

where K_{ina} is the **ionisation constant of the indicator.** If the activity coefficients are assumed to be unity—a not entirely justifiable assumption as will be evident from the ensuing discussion—equation (iii) reduces to the simplified "concentration form":

$$[H^+] = \frac{[HIn]}{[In^-]} \times K_{ina} = \frac{[\text{Unionised form}]}{[\text{Ionised form}]} \times K_{ina} \qquad (iiia).$$

The actual colour of the indicator, which depends upon the ratio of the concentrations of the ionised and unionised forms, is thus directly related to the hydrogen ion concentration. Equation (iii*a*) (the simplified or "classical" form) may be written logarithmically:

$$pH = \log \frac{[In^-]}{[HIn]} + pK_{ina} \qquad (iv).$$

For a base indicator an exactly analogous expression to (iii) may be deduced, which in its simplified form is:

$$[OH^-] = \frac{[InOH]}{[In^+]} \times K_{inb} \qquad (v),$$

where K_{inb} is the corresponding base dissociation constant. This may be written :

$$[H^+] = \frac{K_w \,.\, [In^+]}{K_{inb} \,.\, [InOH]} \qquad (vi),$$

since $K_w = [H^+] \times [OH^-]$ (approximately).

The work of Hantzsch and others has shown that Ostwald's simple theory of the colour change of indicators requires revision. The newer theory, however, leads to equations similar to the above. We can no longer regard the colour change as being due to ionisation alone, for it has been shown that an indicator consists of two or more different tautomeric forms possessing different constitutional formulae and different colours ; one of the forms is a non-electrolyte (a **pseudo acid** or **pseudo base**), the other form being an acid or a base. The ions of the true acid or true base possess the same colour as undissociated form of the same structure. We can illustrate this by reference to phenolphthalein, the changes for which are characteristic of all phthalein indicators (Fig. 1-4).

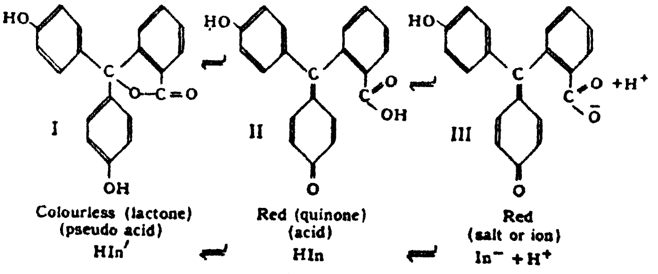

FIG. 1-4.

In the solid state or in acid solution, it exists chiefly as the colourless lactone I. This is in equilibrium in solution with a trace of the tautomeric quinonoid form II,[*] which is an acid since it possesses the carboxyl group —COOH and dissociates to yield the H$^+$ ion and the indicator ion III.

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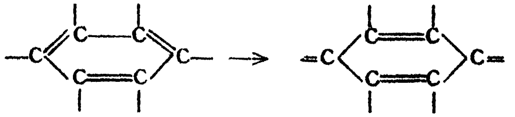
[*] The change from the benzenoid to the quinonoid form is believed to be responsible for the production of colour :



or more probably a state of resonance or mesomerism obtains wherein the coloured ion possesses a structure intermediate between the various possible benzenoid and quinonoid forms.

Consider now an acid or, more correctly, a pseudo-acid indicator in the light of the new theory. Let HIn′ represent the pseudo acid and HIn the acid. Two equilibria must be considered in aqueous solution :

$$\mathrm{HIn'} \rightleftharpoons \mathrm{HIn} \qquad \text{(vii)},$$

and

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-} \qquad \text{(viii)}.$$

Applying the law of mass action to both, we have :

for (vii), $$K_T = a_{\mathrm{HIn}} \,/\, a_{\mathrm{HIn'}} \qquad \text{(ix)};$$

and for (viii), $$K_I = a_{\mathrm{H^+}} \times a_{\mathrm{In^-}} \,/\, a_{\mathrm{HIn}} \qquad \text{(x)}.$$

The ion $\mathrm{In^-}$ has the same colour as the weak acid HIn. In acid solution, *i.e.*, in the presence of excess of $\mathrm{H^+}$ ions, the indicator will exist largely as HIn and HIn′. Now these two forms have different colours, and HIn has the same colour as $\mathrm{In^-}$. The indicator will only be useful if the equilibrium constant for the tautomeric equilibrium (vii) is very small ; then practically the whole of the undissociated indicator will be in the form HIn′. Combining (ix) and (x), we obtain :

$$K_{\mathrm{ina}} = K_T \times K_I = \frac{a_{\mathrm{HIn}}}{a_{\mathrm{HIn'}}} \times \frac{a_{\mathrm{H^+}} \times a_{\mathrm{In^-}}}{a_{\mathrm{HIn}}} = \frac{a_{\mathrm{H^+}} \times a_{\mathrm{In^-}}}{a_{\mathrm{HIn'}}} \qquad \text{(xi)}$$

where K_{ina} is the **apparent dissociation constant** of the indicator. We have assumed that the activity (and therefore the concentration) of HIn′ to be very much greater than that of HIn, hence $a_{\mathrm{HIn'}}$ is virtually the activity of all the indicator not in the salt or ionic form, and the expression (xi) is identical with (ii) deduced from the Ostwald theory.

Equation (xi) may be written in the following forms :

$$K_{\mathrm{ina}} = \frac{[\mathrm{H^+}] \times [\mathrm{In^-}]}{[\mathrm{HIn'}]} \times \frac{f_{\mathrm{H^+}} \times f_{\mathrm{In^-}}}{f_{\mathrm{HIn'}}} \qquad \text{(xi}a\text{)};$$

$$f_{\mathrm{H^+}}\,[\mathrm{H^+}] = \frac{[\mathrm{HIn'}]}{[\mathrm{In^-}]} \times K_{\mathrm{ina}} \times \frac{f_{\mathrm{HIn'}}}{f_{\mathrm{In^-}}}$$

$$= \frac{[\text{Form with ``acid'' colour}]}{[\text{Form with ``alkaline'' colour}]} \times K_{\mathrm{ina}} \times \frac{f_{\mathrm{HIn'}}}{f_{\mathrm{In^-}}} \qquad \text{(xii)};$$

$$\text{or } p\mathrm{H} = \log\,[\mathrm{In^-}] \,/\, [\mathrm{HIn'}] + pK_{\mathrm{ina}} + \log f_{\mathrm{In^-}} \,/\, f_{\mathrm{HIn'}},$$

$$= \log\,[\mathrm{In^-}] \,/\, [\mathrm{HIn'}] + pK_{\mathrm{ina}} + \log f_{\mathrm{In^-}} \qquad \text{(xiii)},$$

since $p\mathrm{H} = -\log f_{\mathrm{H^+}}\,[\mathrm{H^+}]$ and $f_{\mathrm{HIn'}}$ may be regarded as constant.

If the activity coefficient of the indicator anion may be expressed by the usual equation (Section **I, 20**), it follows that:

$$pH = pK_{ina} + \log [In^-] / [HIn'] - 0{\cdot}505\, z_i^2\, \mu^{0\cdot5} + C\mu \quad (xiiia).$$

In dilute solution ($\mu \ngtr 0{\cdot}01$) the term $C\mu$ may be neglected, and the equation reduces to:

$$pH = pK_{ina} + \log [In^-] / [HIn'] - 0{\cdot}505\, z_i^2 \mu^{0\cdot5} \quad (xiiib).$$

The colour of an indicator is determined by the ratio of the *concentrations* of HIn′ and In⁻ (the pseudo acid and the ionised form), but the actual *p*H will depend upon the ionic strength of the solution (equation xiii*b*). Hence when making a colour comparison for the determination of the *p*H of a solution not only must the indicator concentration be the same in the two solutions, but the ionic strengths must be equal or approximately, equal. Equations (xiii*a*) and (xiii*b*) incidentally provide an explanation of the so-called " salt effect " which is observed with indicators.

For many practical purposes it is sufficient to write equation (xiii*a*) in the form:

$$pH = pK_{ina} + \log [In^-] / [HIn'] \quad (xiiic),$$

provided the influence of ionic strength be borne in mind. As already mentioned the colour of an indicator is determined by the ratio of the concentrations of the " acid " and " alkaline " forms. Both forms are present at any hydrogen ion concentration. It must be realised, however, that the human eye has a limited ability to detect either of the two colours when one of them predominates. Experience shows that the solution will appear to have the " acid " colour, *i.e.*, of HIn′, up to the ratio of $[HIn']$ to $[In^-]$ of approximately 10, and the " alkaline " colour, *i.e.*, of In⁻, up to a similar ratio of $[In^-]$ to $[HIn']$ of approximately 10. Thus only the " acid " colour will be visible when $[HIn'] / [In^-] < 10$, the corresponding limit of *p*H given by equation (xiii*c*) is:

$$pH = pK_{ina} - 1;$$

only the " alkaline " colour will be visible when $[In^-] / [HIn'] < 10$, and the corresponding limit of *p*H is:

$$pH = pK_{ina} + 1.$$

The colour change interval is accordingly $pH = pK_{ina} \pm 1$, *i.e.*, over approximately two *p*H units. Within this range the indicator will appear to change from one colour to the other. The change will be gradual, since it depends upon the ratio of the concentrations of the two coloured forms (pseudo acid and ionised). When the pH of the solution is equal to the apparent dissociation constant of the indicator pK_{ina}, the ratio [HIn′] to [In⁻] becomes equal to 1, and the indicator will have a colour due to an equal mixture of the " acid " and " alkaline " forms. This is sometimes known as the *middle tint* of the indicator. This applies strictly only if the two colours are of equal intensity. In one form is more intensely coloured than the other or if the eye is more sensitive to one colour than the other, then the middle tint will be slightly displaced along the pH range of the indicator.

For an indicator base we have, according to the modified theory, the two equilibria :

$$\mathrm{In'OH} \rightleftharpoons \mathrm{InOH} \qquad \text{(xiv)},$$

and

$$\mathrm{InOH} \rightleftharpoons \mathrm{In^+} + \mathrm{OH^-} \qquad \text{(xv)}.$$

The following equation may be deduced along similar lines to that described for an indicator acid :

$$f_{\mathrm{OH^-}}\,[\mathrm{OH^-}] = \frac{[\mathrm{In'OH}]}{[\mathrm{In^+}]} \times K_{inb} \times \frac{f_{\mathrm{In'OH}}}{f_{\mathrm{In^+}}}$$

$$= \frac{[\text{Form with " alkaline " colour}]}{[\text{Form with " acid " colour}]} \times K_{inb} \times \frac{f_{\mathrm{In'OH}}}{f_{\mathrm{In^+}}} \qquad \text{(xv)},$$

where K_{inb} is the apparent dissociation constant of the base. Remembering that $K_w = f_{\mathrm{H^+}}\,[\mathrm{H^+}] \times f_{\mathrm{OH^-}}\,[\mathrm{OH^-}]$, we may write :

$$f_{\mathrm{H^+}}\,[\mathrm{H^+}] = \frac{K_w}{K_{inb}} \times \frac{[\mathrm{In^+}]}{[\mathrm{In'OH}]} \times \frac{f_{\mathrm{In^+}}}{f_{\mathrm{In'OH}}} \qquad \text{(xvi)}.$$

The equation is of the same form as (xii) since the ratio of the two constants may be replaced by a new constant $K_{inb'}$.

The above theory applies only to a monobasic acid or to a monoacid base. Complications arise if two such changes are possible, and the transition range may be increased.

The apparent ionisation constant of an indicator may be determined approximately by finding either the pH of a solution (Section **I, 17**) containing it when it shows its middle tint, or by finding the range of hydrogen ion concentration in which definite colour changes are observed ; the pH of such a solution lies within the limits pK_{ina} (or pK_{inb}) $\pm$ 1. A more accurate method depends upon the determination of the fraction of the indicator (*e.g.*, [In⁻] / [HIn′]) which has changed colour in a series of solutions of known pH (buffer solutions—Section **I, 20**) ; the approximate apparent dissociation constants may then be calculated from equations (xii) or (xvi), the activity coefficients being assumed to be unity. With a one colour indicator the colour intensity is measured, *e.g.*, by means of a colorimetric or spectrophotometric method, in a series of solutions of equal concentration of indicator and different values of pH. For an indicator of the phenolphthalein type, the standard of comparison will be a solution containing an appreciable excess of alkali: this will correspond to a value of $[In^-]$ equal to the total indicator concentration. With a two-colour indicator, various modifications must be introduced, which cannot, however, be discussed here. In some cases, *e.g.*, p-nitrophenol and methyl orange, the constants may be determined by conductance measurements or by a study of the hydrolysis of salts. Some approximate values of the apparent dissociation constants of indicators, which we may term *indicator constants* K_{in} are given in Table X. This Table contains a selected list of indicators suitable for volumetric analysis and also for the colorimetric determination of pH (Section **V, 6**).

TABLE X. COLOUR CHANGES AND pH RANGE OF CERTAIN INDICATORS.

Indicator	*Chemical Name*	p*H Range*	*Colour in Acid Solution*	*Colour in Alkaline Solution*	pK_{in}
Brilliant cresyl blue (acid)	Amino-diethyl-amino-methyl diphenazonium chloride	0·0– 1·0	Red-orange	Blue	
Cresol red (acid)	α-Cresolsulphone-phthalein	0·2– 1·8	Red	Yellow	
Quinaldine red	α-(p-dimethyl-amino - phenyl-ethylene) - quinoline ethiodide	1·0– 2·0	Colourless	Red	
Thymol blue (acid)	Thymol-sulphone-phthalein	1·2– 2·8	Red	Yellow	1·7
Tropaeolin OO	Diphenylamino - p benzene - sodium sulphonate	1·3– 3·0	Red	Yellow	
Meta-cresol purple	m - Cresol - sulphone-phthalein	1·2– 2·8	Red	Yellow	
Bromo-phenol blue	Tetrabromophenol-sulphone - phthalein	2·8– 4·6	Yellow	Blue	4·0
Methyl yellow	Dimethylamino-azo-benzene	2·9– 4·0	Red	Yellow	
Methyl orange	Dimethylamino-azo-benzene sodium sulphonate	3·1– 4·4	Red	Yellow	3·7

TABLE X—*continued.*

Indicator	*Chemical Name*	pH *Ranbe*	*Colour in Acid Solution*	*Colour in Alkaline Solution*	pK_{in}
Congo red	Diphenyl - dis - azo - α - naphthylamine - 4 - sulphonic acid	3·0– 5·0	Violet	Red	
Bromo-cresol green	Tetrabromo - *m* - cresol - sulphonephthalein	3·8– 5·4	Yellow	Blue	4·7
Methyl red	*o*-Carboxybenzene-azo - dimethylaniline	4·2– 6·3	Red	Yellow	5·1
Chloro-phenol red	Dichloro-phenol-sulphone - phthalein	4·8 –6·4	Yellow	Red	6·0
p-Nitrophenol	*p*-Nitrophenol	5·6– 7·6	Colourless	Yellow	7·1
Bromo -cresol purple	Dibromo-*o*-cresol-sulphone - phthalein	5·2– 6·8	Yellow	Purple	6·3
Azolitmin (litmus)	—	5·0– 8·0	Red	Blue	
Bromo-thymol blue	Dibromo - thymol-sulphone - phthalein	6·0– 7·6	Yellow	Blue	7·0
Neutral red	Amino - dimethyl-amino - tolu - phenazonium chloride	6·8 –8·0	Red	Orange	
Phenol red	Phenol - sulphone-phthalein	6·8– 8·4	Yellow	Red	7·9
Cresol red (base)	*o*-Cresol-sulphone-phthalein	7·2– 8·8	Yellow	Red	8·3
α-Naphthol-phthalein	α-Naphtholphthalein	7·3– 8·7	Yellow	Blue	8·4
Thymol blue (base)	Thymol-sulphone-phthalein	8·0– 9·6	Yellow	Blue	8·9
Phenolphthalein	Phenolphthalein	8·3–10·0	Colourless	Red	9·6
Turmeric	—	8·0–10·0	Yellow	Orange	
Thymolphthalein	Thymolphthalein	9·3–10·5	Colourless	Blue	9·2
Alizarine yellow R	*p* - Nitrobenzene - azo - salicylic acid	10·1–12·0	Yellow	Orange red	
Brilliant cresyl blue (base)	(see above)	10·8–12·0	Blue	Yellow	
Tropaeolin O	*p* - Sulphobenzene-azo-resorcinol	11·1–12·7	Yellow	Orange	
Nitramine	2 : 4 : 6-Trinitrophenyl - methyl - nitroamine	10·8–13·0	Colourless	Orange-Brown	

It is necessary to draw attention to the *p*H of various types of water which may be encountered in quantitative analysis. Water in equilibrium with the normal atmosphere containing

0·03 per cent by volume of carbon dioxide has a *p*H of about 5·7 ; very carefully prepared conductivity water has a *p*H close to 7 ; water saturated with carbon dioxide under a pressure of one atmosphere has a *p*H of about 3·7 at 25°C. The analyst may therefore be dealing, according to the conditions that prevail in the laboratory, with water having a *p*H between the two extremes *p*H 3·7 to *p*H 7. Hence for indicators which show their alkaline colours at *p*H values above 4·5, the effect of carbon dioxide introduced during a titration either from the atmosphere or from the titrating solutions must be seriously considered. This subject is discussed again later (Section **I, 32**).

The colour change intervals of most of the various indicators listed in the Table are represented graphically in Fig. 1-5.

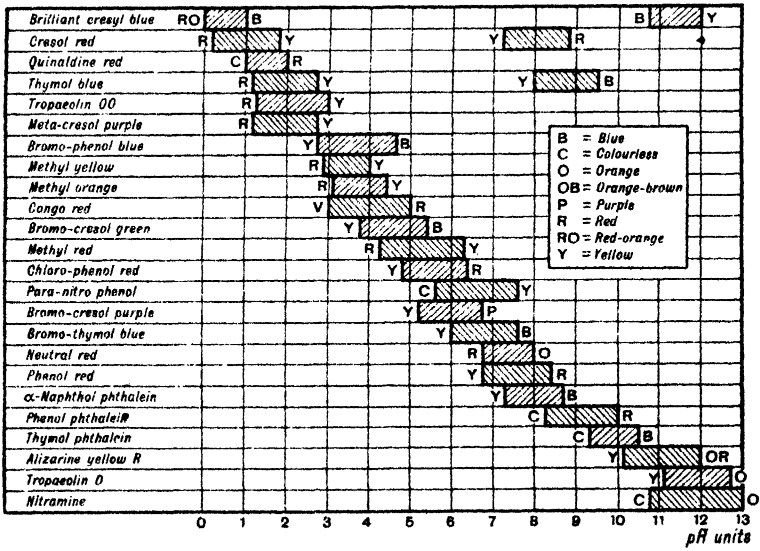


FIG. 1-5

It will be seen that the *p*H range between 0 and 13 is covered by the above indicators.

The indicators at present most used in quantitative analysis are methyl orange (as the simple or "screened" forms—see Section **I, 29**), methyl red and phenolphthalein. The phthalein indicators merit much more attention than has hitherto been given to them ; this would be the case if their many advantages, particularly their sharp colour changes and slight sensitivity to carbon dioxide, were more widely realised.

I, 28. Preparation of indicator solutions.—As a rule the stock solution of the indicators contain 0·5 to 1 g. of indicator per litre of solvent. If the substance is soluble in water, *e.g.*, if a sodium salt, water is the solvent ; in most other cases 70 to 90 per cent alcohol is employed. It should now be stated that the new synthetic indicators, particularly the sulphonephthaleins and phthaleins which exhibit brilliant colour changes, may be used with confidence in all those cases where the older ones, largely natural products, were formerly employed.

Methyl orange. This indicator is encountered in commerce either as the free acid or as the sodium salt.

Dissolve 0·5 g. of the free acid in 1 litre of water, and filter the cold solution if a precipitate separates.

Dissolve 0·5 g. of the sodium salt in 1 litre of water, add 15·2 ml. of 0·1*N* hydrochloric acid, and filter, if necessary, when cold.

Methyl red. Dissolve 1 g. of the free acid in 1 litre of hot water, or dissolve in 600 ml. of alcohol and dilute with 400 ml. of water.

Phenolphthalein. Dissolve 5 g. of the reagent in 500 ml. of alcohol and add 500 ml. of water with constant stirring. Filter, if a precipitate forms.

Thymolphthalein. Dissolve 0·4 g. of the reagent in 600 ml. of alcohol and add 400 ml. of water with stirring.

α-Naphtholphthalein. Dissolve 1 g. of the indicator in 500 ml. of alcohol and dilute with 500 ml. of water.

Litmus. Commercial litmus contains, in addition to the colouring matter (azolitmin), varying quantities of calcium carbonate, calcium sulphate, etc. Purification is effected as follows. Digest 10 g. of the commercial substance with 35 ml. of rectified spirit on the water bath for 1 hour and decant the alcohol ; repeat this process twice so that 105 ml. of alcohol are employed in all. Extract the residue several times with water (total volume 175 ml.—the first 25 ml. is discarded as it contains most of the potassium carbonate), and allow to stand for several days. Decant or siphon off the clear extract. This is of suitable concentration for most practical purposes.

As a general rule the use of litmus in quantitative neutralisations should be avoided, for the solution may contain variable amounts of the colouring matter. It is useful for qualitative tests, but then litmus paper is to be preferred to the solution. Such indicators as bromo-cresol purple or bromo-thymol blue, which cover approximately the same *p*H range, are excellent substitutes for litmus; the colour changes are very striking and a pure product can be obtained, so that a uniform solution is assured.

Azolitmin. This is the pure litmus colouring matter and consists largely of the blue potassium salt of (red) azolitmic acid. A solution is prepared by dissolving 1 g. in 1 litre of water. It is not very much more sensitive than good litmus solution.

Sulphonephthaleins. These indicators are usually supplied in the acid form. They are rendered water soluble by adding sufficient sodium hydroxide to neutralise the potential sulphonic acid group. 1 gram of the indicator is triturated in a clean glass mortar with the appropriate quantity of 0·1*N* sodium hydroxide solution, and then diluted with water to 1 litre. The following volumes of 0·1*N* sodium hydroxide are required for 1 g. of the indicators: bromo-phenol blue, 15·0 ml.; bromo-cresol green, 14·4 ml.; bromo-cresol purple, 18·6 ml.; chloro-phenol red, 23·6 ml.; bromo-thymol blue, 16·0 ml.; phenol red, 28·4 ml.; thymol blue, 21·5 ml.; cresol red, 26·2 ml.; meta-cresol purple, 26·2 ml.

Quinaldinic acid. Dissolve 1 g. in 100 ml. of rectified spirit.

Methyl yellow, neutral red, and congo red. Dissolve 1 g. of the indicator in 1 litre of 80 per cent alcohol. Congo red may also be dissolved in water.

***p*-Nitrophenol.** Dissolve 2 g. of the solid in 1 litre of water.

Alizarine yellow R. Dissolve 0·5 g. of the indicator in 1 litre of rectified spirit.

Tropaeolin O and Tropaeolin OO. Dissolve 1 g. of the solid in 1 litre of water.

Many of the indicator solutions are available commercially already prepared for use. These should be bought from the actual chemical manufacturers, who will usually supply full details as to the method of preparation, concentration of the solution, etc.

I, 29. Mixed indicators.—With some indicators, *e.g.*, methyl orange, the colour change is not easily detectable, particularly in artificial light. A sharper and more pronounced colour change may often be obtained by using a suitable mixture of the indicator and an indifferent dye. Thus for methyl orange, Moerk (1921) used a mixture of 1 g. of methyl orange and 2·5 g. of indigo carmine dissolved in 1 litre of water; the colour change from the alkaline to the acid side is yellowish-green → grey → violet, the grey stage being reached at *p*H 4. Hickman and Linstead (1922) obtained a somewhat better effect by dissolving a mixture of 1 g. of methyl orange and 1·4 g. of xylene cyanol FF* in 500 ml. of 50 per cent alcohol; here the colour change from the alkaline to the acid side is green → grey → magenta, the middle grey stage being obtained at *p*H 3·8. The above is an example of a **screened indicator,** and the solution is sometimes known as " screened " methyl orange.

For some purposes it is desirable to have a sharp colour change over a narrow and selected range of hydrogen ion concentration; this is not easily seen with an ordinary indicator since the colour change usually extends over two units of *p*H. The result may, however, be achieved by the use of a suitable mixture of indicators. Four examples will be given.

(*a*) A mixture of equal parts of neutral red (0·1% solution in alcohol) and methylene blue (0·1% solution in alcohol) gives a sharp colour change from violet-blue to green in passing from acid to alkaline solution at *p*H 7. This indicator may be employed to titrate acetic acid with ammonia solution or *vice versa*. Both acid and base are approximately of the same strength, hence the equivalence point will be at a *p*H of *ca*. 7 (Section **I, 35**); owing to the extended hydrolysis and the flat nature of the titration curve (see Section **I, 35**), the titration cannot be performed except with an indicator of very narrow range.

(*b*) A mixture of equal parts of methyl orange or of methyl yellow (0·1% solution in alcohol) and methylene blue (0·1% solution in alcohol) may be used in the titration of the very weak base pyridine and a strong acid; in this case also the

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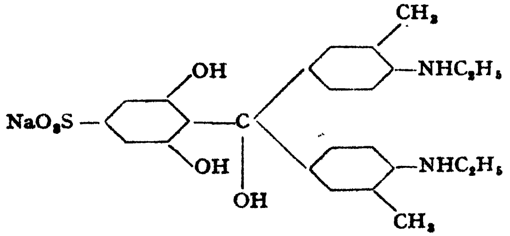
* The constitution is :



titration curve is very flat. This indicator is also useful for other somewhat stronger bases and strong acids.

(*c*) A mixture of phenolphthalein (2 parts of 0·1% solution in 50% alcohol) and α-naphtholphthalein (1 part of 0·1% solution in 50% alcohol) passes from pale rose through green to violet at *p*H = 9·6. The mixed indicator is suitable for the titration of phosphoric acid to the dibasic stage ($K_2 = 6{\cdot}2 \times 10^{-8}$; equivalence point at *p*H = *ca.* 9·7).

Phenolphthalein, which was previously used, is not so satisfactory since its *p*H range is 8·3 to 10 and the titration curve is relatively flat (Section **I, 36**).

(*d*) A mixture of thymol blue (6 parts of 0·1% aqueous solution) and cresol red (1 part of 0·1% aqueous solution) is violet at *p*H 8·4, blue at *p*H 8·3, and rose at *p*H 8·2. It has been recommended by Simpson (1924) for the titration of carbonate to the bicarbonate stage.

I, 30. Universal or multiple range indicators.—By suitably mixing certain indicators the colour change may be made to extend over a considerable portion of the *p*H range. Such mixtures are usually called "**universal indicators.**" They are not suitable for quantitative titrations, but may be employed for the determination of the approximate *p*H of a solution by the colorimetric method. Bogen (1927) gives the following details: dissolve 0·1 g. of phenolphthalein, 0·2 g. of methyl red, 0·3 g. of methyl yellow, 0·4 g. of bromothymol blue, and 0·5 g. of thymol blue in 500 ml. of absolute alcohol, and add sufficient sodium hydroxide solution until the colour is yellow. The colour changes are as follows: *p*H 2, red; *p*H 4, orange; *p*H 6, yellow; *p*H 8, green; *p*H 10, blue.

The following recipe is due to T. B. Smith (1929). Dissolve 0·05 g. of methyl orange, 0·15 g. of methyl red, 0·3 g. of bromo-thymol blue, and 0·35 g. of phenolphthalein in 1 litre of 66 per cent alcohol. The colour changes are: *p*H up to 3, red; *p*H 4, orange-red; *p*H 5, orange; *p*H 6, yellow; *p*H 7, yellowish green; *p*H 8, greenish-blue; *p*H 9, blue; *p*H 10, violet; *p*H 11, reddish-violet. Several "universal indicators" are available commercially: that of the British Drug Houses, London, is most widely used.

Colorimetric determination of pH. This is discussed fully in Chapter V.

I, 31. Neutralisation curves.—An insight into the mechanism of neutralisation processes is obtained by studying the changes in the hydrogen ion concentration during the course of the appropriate titration. The change in *p*H in the neighbourhood of the equivalence point is of the greatest importance as it enables us to select an indicator which will give the smallest titration error. The curve obtained by plotting *p*H as ordinates against the percentage of acid neutralised (or the number of ml. of alkali added) as abscissae is known as the **neutralisation** (or, more generally, the **titration**) **curve.** This may be determined experimentally by an estimation of the *p*H at various stages during the titration by an electrometric method (Section **I, 52**), or it may be computed approximately with the aid of the theoretical principles that we have already studied. We shall, for the present, adopt the latter method.

I, 32. Neutralisation of a strong acid and a strong base.— We shall assume that both the acid and the base are completely dissociated and that the activity coefficients of the ions are unity in order to calculate the change of *p*H during the course of the neutralisation of the strong acid and the strong base, or *vice versa*, at the laboratory temperature. For simplicity of calculation we shall start with 100 ml. of, say, N hydrochloric acid and add N sodium hydroxide solution. The *p*H of N hydrochloric acid is 0. When 50 ml. of the N base have been added, 50 ml. of un-neutralised N acid will be present in a total volume of 150 ml.;

$[H^+]$ will therefore be $50 \times 1/150 = 3{\cdot}33 \times 10^{-1}$, or $pH = 0{\cdot}48$.

For 75 ml. of base, $[H^+] = 25 \times 1/175 = 1{\cdot}43 \times 10^{-1}$, $pH = 0{\cdot}94$.

For 90 ml. of base, $[H^+] = 10 \times 1/190 = 5{\cdot}27 \times 10^{-2}$, $pH = 1{\cdot}3$.

For 98 ml. of base, $[H^+] = 2 \times 1/198 = 1{\cdot}01 \times 10^{-2}$, $pH = 2{\cdot}0$.

For 99 ml. of base, $[H^+] = 1 \times 1/199 = 5{\cdot}03 \times 10^{-3}$, $pH = 2{\cdot}3$.

For 99·9 ml. of base, $[H^+] = 0{\cdot}1 \times 1/199{\cdot}9 = 5{\cdot}01 \times 10^{-4}$, $pH = 3{\cdot}3$.

Upon the addition of 100 ml. of base, the *p*H will change sharply to 7, the equivalence point, provided carbon dioxide is absent; the resultant solution is equivalent to one of sodium chloride.

With 100·1 ml. of base, $[OH^-] = 0{\cdot}1/200{\cdot}1 = 5{\cdot}00 \times 10^{-4}$, $pOH = 3{\cdot}3$ and $pH = 10{\cdot}7$.

With 101 ml. of base, $[OH^-] = 1/201 = 5{\cdot}00 \times 10^{-3}$, $pOH = 2{\cdot}3$, and $pH = 11.7$.

These results show that as the titration proceeds, the *p*H rises slowly, but between the addition of 99·9 ml. and 100·1 ml. of alkali, the *p*H of the solution rises from 3·3 to 10·7, *i.e.*, in the vicinity of the equivalence point the rate of change of *p*H of the solution is very rapid.

The complete results, extended to 200 ml. of alkali, are collected in Table XI; this also includes the figures for 0·1*N* and 0·01*N* solutions of acid and base respectively. The additions of alkali have been extended in all three cases to 200 ml.; it is evident that the range from 200 ml. to 100 ml. and beyond represents the reverse titration of 100 ml. of alkali with the acid in the presence of the non-hydrolysed sodium chloride solution. The data in the Table are presented graphically in Fig. 1–6.

TABLE XI. *p*H DURING TITRATION OF 100 ML. OF HCl WITH NaOH OF EQUAL NORMALITY.

Ml. of NaOH added	*N solution* p*H*	0·1*N solution* p*H*	0·01*N solution* p*H*
0	0·0	1·0	2·0
50	0·5	1·5	2·5
75	0·8	1·8	2·8
90	1·3	2·3	3·3
98	2·0	3·0	4·0
99	2·3	3·3	4·3
99·5	2·6	3·6	4·6
99·8	3·0	4·0	5·0
99·9	3·3	4·3	5·3
100·0	7·0	7·0	7·0
100·1	10·7	9·7	8·7
100·2	11·0	10·0	9·0
100·5	11·4	10·4	9·4
101	11·7	10·7	9·7
102	12·0	11·0	10·0
110	12·7	11·7	10·7
125	13·2	12·2	11·2
150	13·5	12·5	11·5
200	14·0	13·0	12·0

In quantitative analysis we are especially interested in the changes of *p*H near the equivalence point. This part of Fig. 1–6 is accordingly shown on a larger scale in Fig. 1–7, on which are also indicated the colour change intervals of some of the common indicators.

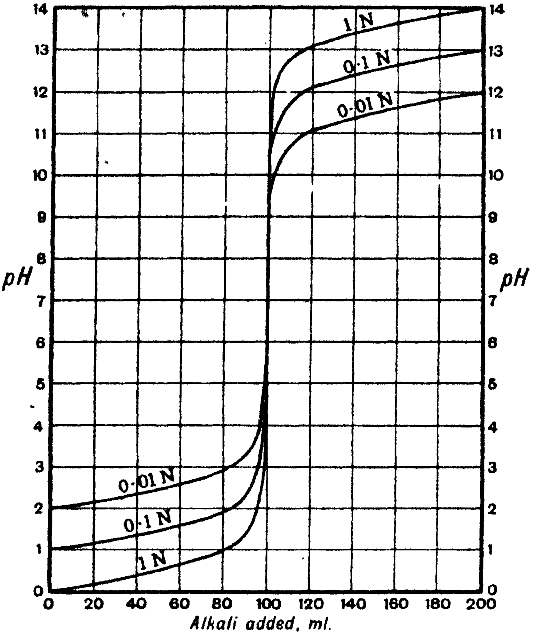


FIG. 1-6. Neutralisation Curves of 100 ml. of HCl with NaOH of same Normality (Calculated).

With N *solutions,* it is evident that any indicator with an effective range between *p*H 3 and 10·5 may be used. The colour change will be sharp and the titration error negligible.

With 0·1N *solutions,* the ideal *p*H range for an indicator is limited to 4·5—9·5. Methyl orange will exist chiefly in the alkaline form when 99·8 ml. of alkali have been added and the titration error will be 0·2 per cent which is negligibly small for most practical purposes; it is therefore advisable to add sodium hydroxide solution until the indicator is present completely in the alkaline form. The titration error is also negligibly small with phenolphthalein.

With 0·01N *solutions,* the ideal *p*H range is still further limited to 5·5—8·5; such indicators as methyl red, bromothymol blue or phenol red will be suitable. The titration error for methyl orange will be 1 to 2 per cent.

The above considerations apply to solutions which do not contain carbon dioxide. In practice, carbon dioxide is usually present (compare Section **I, 27**); it may be derived from the small quantity of carbonate in the sodium hydroxide

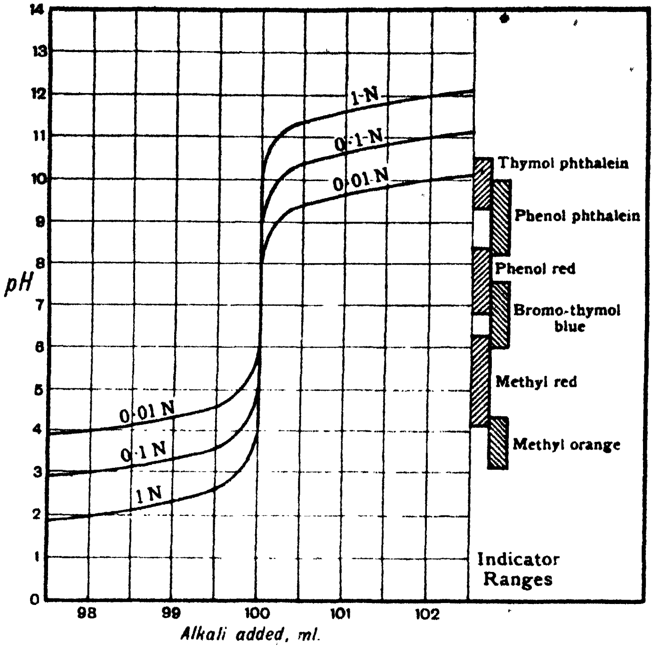


FIG. 1-7. Neutralisation Curves of 100 ml. of HCl with NaOH of same Normality in Vicinity of Equivalence Point (Calculated).

and/or from the atmosphere. The gas is in equilibrium with carbonic acid, of which both stages of ionisation are weak. This will introduce a small error when indicators of high *p*H range (above *p*H 5) are used, *e.g.*, phenolphthalein or thymolphthalein. More acid indicators, such as methyl orange and methyl yellow, are unaffected by carbonic acid. Kolthoff has calculated that the difference in the amounts of sodium hydroxide solution used with methyl orange and phenolphthalein is not greater than 0·15 to 0·2 ml. of 0·1*N* sodium hydroxide when 100 ml. of 0·1*N* hydrochloric acid are titrated. A method of eliminating this error, other than that of selecting an indicator with a *p*H range below *p*H 5, is to boil the solution while still acid and to continue the titration with the cold solution. Boiling the solution is particularly efficacious when titrating dilute (*e.g.*, 0·01*N*) solutions.

I, 33. Neutralisation of a weak acid with a strong base.—We shall confine our attention to 0·1*N* solutions; other concentrations can be treated analogously. Let us study the neutralisation of 100 ml. of 0·1*N* acetic acid with 0·1*N* sodium hydroxide solution. The *p*H of the solution at the equivalence point is given by (Section **I, 19**) :

$$\begin{aligned} pH &= 1/2\, pK_w + 1/2 pK_a + 1/2 \log c, \\ &= 7 \quad + 2{\cdot}37 \quad + 1/2\,(-1) = 8{\cdot}87. \end{aligned}$$

For other concentrations, we may employ the approximate mass action expression :

$$[H^+] \times [C_2H_3O_2^-] \,/\, [H.C_2H_3O_2] = K_a \qquad \text{(i)},$$

or $$[H^+] = [H.C_2H_3O_2] \times K_a \,/\, [C_2H_3O_2^-],$$

or $$pH = \log\,[\text{Salt}] \,/\, [\text{Acid}] + pK_a \qquad \text{(ii)}.$$

The concentration of the acid at any point is taken as equal to the concentration of the acid that has not yet been neutralised, and the concentration of the salt is assumed equal to the concentration of alkali added. These approximations are not valid at the beginning of the neutralisation, but since we are interested only in the *p*H change near the stoichiometric point, the subsequent argument is unaffected.

The initial *p*H of 0·1*N* acetic acid is computed from equation (i) ; the dissociation of the acid is relatively so small that it may be neglected in expressing the concentration of acetic acid. Hence from equation (i) :

$$[H^+] \times [C_2H_3O_2^-] \,/\, [H.C_2H_3O_2] = 1{\cdot}82 \times 10^{-5},$$

or $$[H^+]^2 \,/\, 0{\cdot}1 = 1{\cdot}82 \times 10^{-5},$$

or $$[H^+] = \sqrt{1{\cdot}82 \times 10^{-6}} = 1{\cdot}35 \times 10^{-3},$$

or $$pH = 2{\cdot}87.$$

When 50 ml. of 0·1*N* alkali have been added,

$$\begin{aligned} [\text{Salt}] &= 50 \times 1{\cdot}1/150 = 1{\cdot}33 \times 10^{-2}, \\ \text{and } [\text{Acid}] &= 50 \times 0{\cdot}1/150 = 1{\cdot}33 \times 10^{-2}, \\ pH &= \log\,(1{\cdot}33 \times 10^{-2}/1{\cdot}33 \times 10^{-2}) + 4{\cdot}74, \\ &= 4{\cdot}74. \end{aligned}$$

The *p*H values at other points on the titration curve are similarly calculated. After the equivalence point has been passed, the solution contains excess of OH^- ions which will repress the hydrolysis of the salt ; the *p*H may be assumed, with sufficient accuracy for our purpose, to be that due to the excess of base present so that in this region the titration curve will almost coincide with that for 0·1*N* hydrochloric acid (Fig. 1-6 and Table XI). All the results are collected in Table XII, and are depicted graphically in Fig. 1-8. The results for the titration of 100 ml. of 0·1N solution of a weaker acid (K_a = 1 × 10^{-7}) with 0·1N sodium hydroxide at the laboratory temperature are also included.

Table XII. Neutralisation of 100 ml. of 0·1N Acetic Acid (K_A = 1·82 × 10^{-5}) and of 100 ml. of 0·1N HA (K_a = 1 × 10^{-7}) with 0·1N Sodium Hydroxide

Ml. of 0·1 N *NaOH used*	0·1N *Acetic Acid* p*H*	0·1N *HA* (K_a = 1 × 10^{-7}) p*H*
0	2·9	4·0
10	3·8	6·0
25	4·3	6·5
50	4·7	7·0
90	5·7	8·0
99·0	6·7	9·0
99·5	7·0	9·3
99·8	7·4	9·7
99·9	7·7	9·8
100·0	8·9	10·0

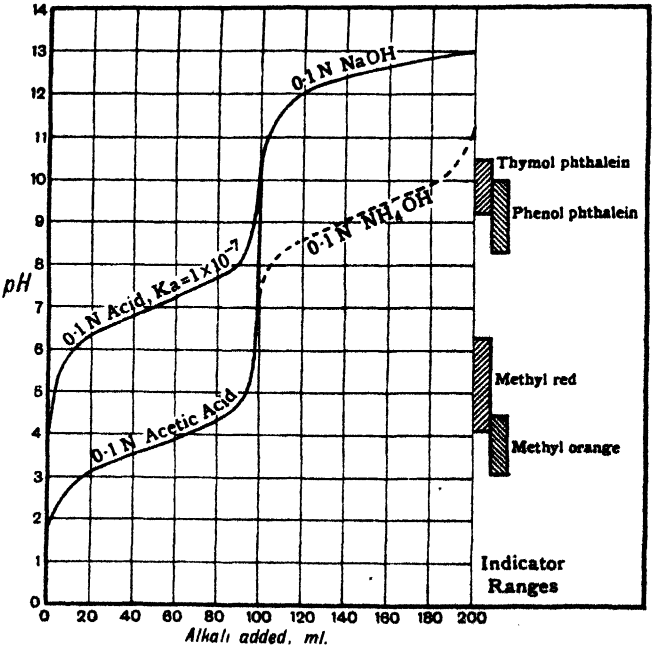


Fig. 1-8. Neutralisation Curves of 0·1N Acetic Acid and of 0·1N Acid (K_a = 1 × 10^{-7}) with 0·1N Sodium Hydroxide (Calculated).

For $0{\cdot}1N$ acetic acid and $0{\cdot}1N$ sodium hydroxide, it is evident from the titration curve that neither methyl orange nor methyl red can be used as indicators. The equivalence point is at pH 8·9, and it is necessary to use an indicator with a pH range on the slightly alkaline side, such as phenolphthalein, thymolphthalein or thymol blue (pH range, as base, 8·0—9·6). For the acid with $K_a = 10^{-7}$, the equivalence point is at $p\text{H} = 10$, but here the rate of change of pH in the neighbourhood of the stoichiometric point is very much less pronounced owing to considerable hydrolysis. Phenolphthalein will commence to change colour after about 92 ml. of alkali have been added and this change will occur to the equivalence point ; thus the end point will not be sharp and the titration error will be appreciable. With thymolphthalein, however, the colour change covers the pH range 9·3—10·5 ; this indicator may be used, the end point will be more sharp than for phenolphthalein, but nevertheless somewhat gradual, and the titration error will be about 0·2 per cent. Acids that have dissociation constants less than 10^{-7} cannot be satisfactorily titrated in $0{\cdot}1N$ solution with a simple indicator.

In general, it may be stated that weak acids ($K_a > 5 \times 10^{-6}$) should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators.

I, 34. Neutralisation of a weak base with a strong acid.— We may illustrate this case by the titration of 100 ml. of $0{\cdot}1N$ ammonium hydroxide ($K_b = 1{\cdot}8 \times 10^{-5}$) with $0{\cdot}1N$ hydrochloric acid at the ordinary laboratory temperature. The pH of the solution at the equivalence point is given by the equation (Section **I, 19**) :

$$\begin{aligned} p\text{H} &= 1/2K_w - 1/2\,pK_b - 1/2\log c, \\ &= 7 \quad - 2{\cdot}37 \quad - 1/2\,(-1) = \mathit{5{\cdot}13}. \end{aligned}$$

For other concentrations, the pH may be calculated in the following manner. Using the approximate mass action expression :

$$[\text{NH}_4^+] \times [\text{OH}^-] \,/\, [\text{NH}_4\text{OH}] = K_b \qquad \text{(i)},$$

or $$[\text{OH}^-] = [\text{NH}_4\text{OH}] \times K_b \,/\, [\text{NH}_4^+] \qquad \text{(ii)},$$

or $$p\text{OH} = \log\,[\text{Salt}] \,/\, [\text{Base}] + pK_b \qquad \text{(iii)},$$

or $$p\text{H} = pK_w - pK_b - \log\,[\text{Salt}] \,/\, [\text{Base}] \qquad \text{(iv)}.$$

The concentration of the base at any point is assumed equal to the concentration of the base that has not been neutralised, and the concentration of the salt is taken as equal to the concentration of acid added. These approximations are not valid at the beginning of the neutralisation, but the error thus introduced is small. After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis of the salt will be repressed, and the subsequent *p*H changes may be assumed, with sufficient accuracy for our purpose, to be those due to the excess of acid present so that in this region the titration curve will almost coincide with that for 0·1*N* sodium hydroxide (Fig. 1-6 and Table XI).

The results computed in the above manner are given in Table XIII, and are represented graphically in Fig. 1-9. The results for the titration of 100 ml. of a 0·1*N* solution of a weaker base ($K_b = 1 \times 10^{-7}$) are also included.

TABLE XIII. NEUTRALISATION OF 100 ML. OF 0·1*N* AMMONIUM HYDROXIDE ($K_b = 1 \cdot 8 \times 10^{-5}$) and of 100 ML. OF 0·1*N* BOH ($K_b = 1 \times 10^{-7}$) with 0·1*N* HYDROCHLORIC ACID.

Ml. of 0·1N *HCl added*	0·1N *Ammonium Hydroxide* p*H*	0·1N *BOH* ($K_b = 1 \times 10^{-7}$) p*H*
0	11·1	10·0
10	10·2	8·0
25	9·8	7·5
50	9·3	7·0
90	8·3	6·1
99·0	7·3	5·0
99·5	7·0	4·7
99·8	6·6	4·3
99·9	6·3	4·0
100·0	5·1	4·0

It is clear that neither thymolphthalein nor phenolphthalein can be employed in the titration of 0·1*N* ammonium hydroxide. The equivalence point is at *p*H 5·1, and it is necessary to use an indicator with a *p*H range on the slightly acid side (3—6·5), such as methyl orange, methyl red, bromo-phenol blue or bromo-cresol green. The last-named indicators may be utilised for the titration of all weak bases ($K_b > 5 \times 10^{-6}$) with strong acids.

For the weak base ($K_b = 1 \times 10^{-7}$), bromo-phenol blue or methyl orange may be used ; no sharp colour change will be obtained with bromo-cresol green or with methyl red, and the titration error will be considerable.

I, 35. Neutralisation of a weak acid with a weak base.— This case is exemplified by the titration of 100 ml. of 0·1*N*

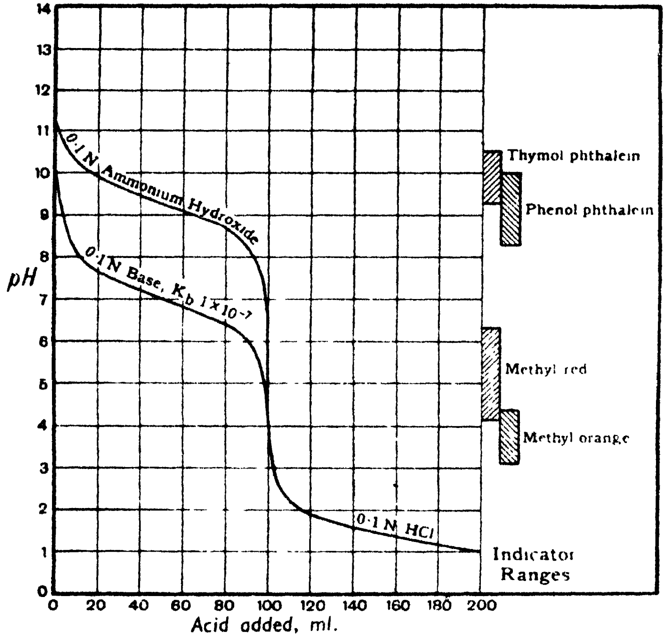


FIG. 1-9. Neutralisation Curves of 100 ml. 0·1N Ammonium Hydroxide ($K_b = 1{\cdot}8 \times 10^{-5}$) and of 0·1$N$ Base ($K_b = 1 \times 10^{-7}$) with 0·1N Hydrochloric Acid.

acetic acid ($K_a = 1{\cdot}8 \times 10^{-5}$) with 0·1$N$ ammonium hydroxide ($K_b = 1{\cdot}8 \times 10^{-5}$). The pH at the equivalence point is given by (Section **I, 19**) :

$$pH = 1/2\ pK_w + 1/2\,pK_a - 1/2pK_b,$$
$$= 7{\cdot}0 + 2{\cdot}37 - 2{\cdot}37 = 7{\cdot}0.$$

The calculation of the neutralisation curve is a little more difficult.* The titration curve for the neutralisation of 100 ml. of 0·1N acetic acid with 0·1N ammonium hydroxide at the laboratory temperature is shown by the dotted line in Fig. 1–8. The chief feature of the curve is that the change of pH near the equivalence point and, indeed, during the whole of the neutralisation curve is very gradual. There is no sudden change in pH, and hence no sharp end point can be found with any simple indicator. A mixed indicator, which exhibits a sharp colour change over a very limited *p*H range, may sometimes be found which is suitable. Thus for acetic acid—ammonia solution titrations, neutral red—methylene blue indicator may be used (see Section **I, 29**). On the whole, it is best to avoid titrations involving *both* a weak acid and a weak base.

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* For details, see, *e.g.*, S. Glasstone, *The Electrochemistry of Solutions*, p. 224 *et seq.* (Methuen and Co., 1937.)

I, 36. Neutralisation of a polybasic acid with a strong base.—The shape of the titration curve will depend upon the relative magnitudes of the various dissociation constants. It is assumed that titrations take place at the ordinary laboratory temperature in solutions of concentration of $0{\cdot}1N$ or stronger. For a dibasic acid, if the difference between the primary and secondary dissociation constants is very large ($K_1/K_2 > 10{,}000$), the solution behaves like a mixture of two acids with constants K_1 and K_2 respectively; the considerations given previously may be applied. Thus for sulphurous acid, $K_1 = 1{\cdot}7 \times 10^{-2}$ and $K_2 = 1{\cdot}0 \times 10^{-7}$, it is evident that there will be a sharp change of *p*H near the first equivalence point, but for the second stage the change will be less pronounced, yet just sufficient for the use of, say, thymolphthalein as indicator (see Fig. 1–8). For carbonic acid, however, for which $K_1 = 4{\cdot}3 \times 10^{-7}$ and $K_2 = 5{\cdot}6 \times 10^{-11}$, only the first stage will be just discernible in the neutralisation curve (see Fig. 1–8); the second stage is far too weak to exhibit any point of inflexion and there is no suitable indicator available for direct titration. As indicator for the primary stage, thymol blue may be used (see Section **I, 34**), although a mixture of thymol blue (3 parts) and cresol red (1 part) (see Section **I, 29**) is more satisfactory; with phenolphthalein the colour change will be somewhat gradual and the titration error may be several per cent.

It can be shown* that the *p*H at the first equivalence point for a dibasic acid is given by

$$[\mathrm{H}^+] = \sqrt{\frac{K_1K_2c}{K_1 + c}}.$$

Provided that the first stage of the acid is weak and that K_1 can be neglected by comparison with c, the concentration of salt present, this expression reduces to $[\mathrm{H}^+] = \sqrt{K_1K_2}$, or $p\mathrm{H} = 1/2\,pK_1 + 1/2\,pK_2$.

With a knowledge of the *p*H at the stoichiometric point and also of the course of the neutralisation curve, it should be an easy matter to select the appropriate indicator for the titration of any dibasic acid for which K_1/K_2 is at least 10^4. For many dibasic acids, however, the two dissociation constants are too close together and it is not possible to differentiate the two stages. If K_2 is not less than about 10^{-7}, all the replaceable hydrogen may be titrated, *e.g.*, sulphuric acid (primary stage—a strong acid), oxalic acid, malonic, succinic, and tartaric acids (for dissociation constants, see Table II, Section **I, 4**).

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* See, for example, S. Glasstone, *The Electrochemistry of Solutions*, 1937, p. 229.

Similar remarks apply to tribasic acids. These may be illustrated by reference to orthophosphoric acid for which $K_1 = 7{\cdot}5 \times 10^{-3}$, $K_2 = 6{\cdot}2 \times 10^{-8}$, and $K_3 = 5 \times 10^{-13}$. Here $K_1/K_2 = 1{\cdot}2 \times 10^5$ and $K_2/K_3 = 1{\cdot}2 \times 10^5$, so that the acid will behave as a mixture of three monobasic acids with the dissociation constants given above. Neutralisation proceeds almost completely to the end of the primary stage before the secondary stage is appreciably affected, and the secondary stage proceeds almost to completion before the tertiary stage is apparent. The pH at the first equivalence point is given approximately by $(1/2\,pK_1 + 1/2\,pK_2) = 4{\cdot}6$, and at the second equivalence point by $(1/2\,pK_2 + 1/2\,pK_3) = 9{\cdot}7$; in the very weak third stage, the curve is very flat and no indicator is available for direct titration. The third equivalence point may be computed approximately from the equation (Section **I, 19**):

$$\begin{aligned} p\mathrm{H} &= 1/2\,pK_w + 1/2\,pK_a + 1/2 \log c. \\ &= 7{\cdot}0 + 6{\cdot}15 + (-0{\cdot}5). \\ &= \mathit{12{\cdot}6} \text{ in } 0{\cdot}1N \text{ solution.} \end{aligned}$$

For the primary stage (phosphoric acid as a monobasic acid), methyl orange, bromo-cresol green or congo red may be used as indicators. The secondary stage of phosphoric acid is very weak (see acid $K_1 = 1 \times 10^{-7}$ in Fig. 1–8) and the only suitable simple indicator is thymolphthalein (see Section **I, 34**); with phenolphthalein the error may be several per cent. A mixed indicator composed of phenolphthalein (2 parts) and α-naphtholphthalein (1 part) is the most satisfactory for the determination of the end point of phosphoric acid as a dibasic acid (see Section **I, 29**). The experimental neutralisation curve of 50 ml. of $0{\cdot}1M$ orthophosphoric acid with $0{\cdot}1N$ potassium hydroxide, determined by electromeric titration, is shown in Fig. 1-10.

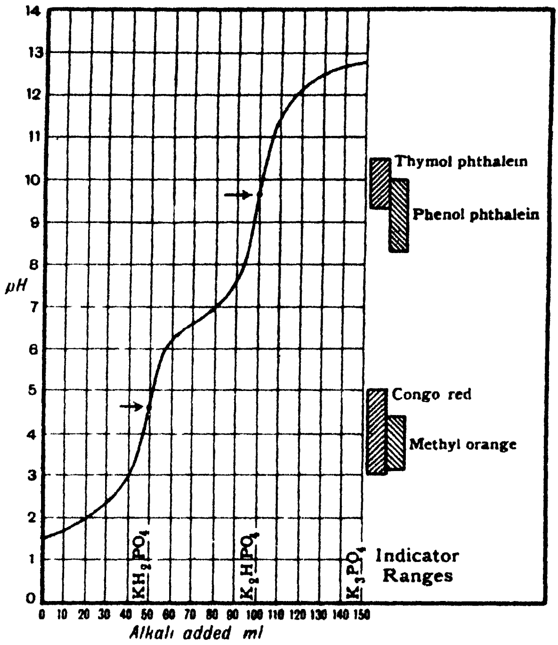

FIG. 1-10. Titration of 50 ml. 0·1*M* H_3PO_4 with 0·1*N KOH*.

There are a number of tribasic acids, *e.g.*, citric acid with $K_1 = 9{\cdot}2 \times 10^{-4}$, $K_2 = 2{\cdot}7 \times 10^{-5}$, $K_3 = 1{\cdot}3 \times 10^{-6}$, the three dissociation constants of which are too close together and for which the three stages cannot consequently be differentiated. If $K_3 >$ *ca.* 10^{-7}, all the replaceable hydrogen may be titrated; the indicator will be determined by the value of K_3.

I, 37. Titration of solutions of hydrolysed salts. Displacement titration.—The examples which are encountered in practice are largely the salts formed from a strong base and a very weak acid, such as potassium cyanide, borax, and sodium carbonate, or the salts derived from a strong acid and a very weak base, for example, aniline hydrochloride. We shall therefore confine our attention to examples of these salts. Both types will be largely hydrolysed in solution.

Titration of potassium cyanide with a strong acid.—Let us consider first the titration of 100 ml. of 0·2*N* potassium cyanide with 0·2*N* hydrochloric acid at the laboratory temperature. The salt is completely dissociated:

$$KCN \rightleftharpoons K^+ + CN^-.$$

The hydrolysis of the salt is represented by :

$$CN^- + H_2O \rightleftharpoons HCN + OH^-.$$

The reaction upon the addition of hydrochloric acid is simply the combination between the H^+ ions from the acid and the OH^- ions produced by hydrolysis :

$$H^+ + OH^- = H_2O.$$

The net result is that the weak hydrocyanic acid has been displaced by the stronger hydrochloric acid :

$$KCN + HCl = HCN + KCl ;$$

the process is therefore often referred to as a **displacement titration.** The pH at the true end point can be calculated from the dissociation constant and the concentration of the weak acid at the equivalence point. Thus in our example, the volume is doubled at the equivalence point, hence the concentration of hydrocyanic acid is 0·1N. K_a for hydrocyanic acid is $7{\cdot}2 \times 10^{-10}$,

$$i.e., \; [H^+] \times [CN^-] \;/\; [HCN] = 7{\cdot}2 \times 10^{-10} ;$$

hence $[H^+] = \sqrt{7{\cdot}2 \times 10^{-10} \times 0{\cdot}1}$, since $[H^+] = [CN^-]$,

or $p\text{H} = 5{\cdot}1.$

If 100·1 ml. of hydrochloric acid are added, the pH will be 4, with 100·2 ml. the pH will be 3·7, with 101 ml. the pH will be 3, etc. There will be a fairly abrupt decrease of pH in the neighbourhood of the equivalence point. If the titration error is not to exceed 0·2 per cent, any indicator covering the pH range 3·7 to 5·1 (and slightly beyond this) may be used ; suitable indicators are bromo-cresol green, methyl orange, bromo-phenol blue, and methyl red.

Titration of borax with a strong acid.—With borax, similar considerations apply. The net result of the displacement titration is given by :

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

Boric acid behaves as a weak monobasic acid with a dissociation constant of 6×10^{-10}. The pH at the equivalence point in the titration of 0·2N borax with 0·2N hydrochloric acid is that due to 0·1N boric acid, *i.e.*, 5·1. Further addition of hydrochloric acid will cause a sharp decrease of pH as in the case of potassium cyanide. Similar indicators may therefore be used.

Titration of sodium carbonate with a strong acid.—The solution of sodium carbonate may be titrated to the bicarbonate stage (*i.e.*, with one equivalent of acid), when the net reaction is:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

The equivalence point for the primary stage of ionisation of carbonic acid is at $pH = (1/2\,pK_1 + 1/2\,pK_2) = 8{\cdot}3$, and we have seen (Section **I, 34**) that *inter alia* thymol blue and, less satisfactorily, phenolphthalein, or a mixed indicator may be employed to detect the end point.

Sodium carbonate solution may also be titrated until all the carbonic acid is displaced (two equivalents of acid). The net reaction is then:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3.$$

The same end point is reached by titrating sodium bicarbonate solution with hydrochloric acid:

$$NaHCO_3 + HCl = NaCl + H_2CO_3.$$

The end point with 100 ml. of $0{\cdot}2N$ sodium bicarbonate and $0{\cdot}2N$ hydrochloric acid may be deduced exactly as described above for potassium cyanide. The pH at the equivalence point is very approximately 3·8 (K_1 for $H_2CO_3 = 4{\cdot}3 \times 10^{-7}$; the secondary ionisation and the loss of carbonic acid, due to escape of carbon dioxide, has been neglected). Suitable indicators are therefore methyl yellow, methyl orange, congo red, and bromo-phenol blue. The experimental titration curve, determined with the hydrogen electrode, for 100 ml. of $0{\cdot}1N$ sodium carbonate and $0{\cdot}1N$ hydrochloric acid is shown in Fig. 1-11.

Salts of weak bases and strong acids, *e.g.*, aniline hydrochloride ($K_b = 4{\cdot}0 \times 10^{-10}$) may be treated in an analogous manner.

I, 38. Choice of indicators in neutralisation reactions.—As a general rule it may be stated that for a titration to be feasible, there should be a change of approximately two units of pH at or near the stoichiometric point produced by the addition of a small volume of the reagent. The pH at the equivalence point may be computed by means of the equations given in Section **I, 19** (see also below); the pH at either side of the equivalence point (0·1—1 ml.) may be calculated as described in the preceding sections, and the difference will indicate whether the change is large enough to permit a sharp

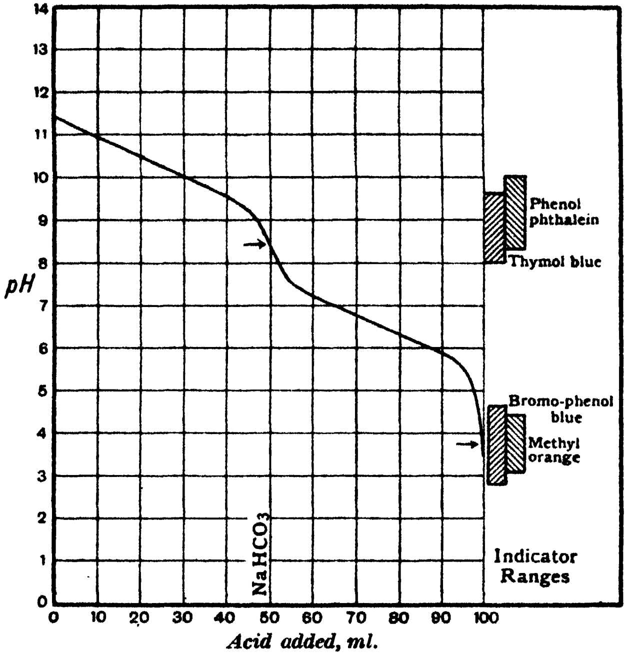

FIG. 1-11. Titration of 100 ml. of 0·1*N* Na_2CO_3 with 0·1*N* HCl.

end point to be determined. Alternatively, the *p*H change on both sides of the equivalence point may be noted from the neutralisation curve determined by electromeric titration (Section **I, 52**). If the *p*H change is satisfactory, an indicator should be selected that changes at or near the equivalence point.

For convenience of reference, we shall summarise the conclusions already deduced from theoretical principles.

Strong acid and strong base. For 0·1*N* solutions or stronger, any indicator may be used which has a range between the limits *p*H 4·5 to *p*H 9·5. With 0·01*N* solutions, the *p*H range is somewhat smaller (5·5 to 8·5). If carbon dioxide is present, the solution should either be boiled whilst still acid and the solution titrated when cold, or an indicator with a range below *p*H 5 be employed.

Weak acid and a strong base. The *p*H at the equivalence point is calculated from the equation:

$$pH = 1/2\ pK_w + 1/2\ pK_a + 1/2 \log c.$$

The pH range for acids with $K_a > 10^{-5}$ is 7—10·5 ; for weaker acids ($K_a > 10^{-6}$), the range is reduced (8—10). The pH range 8—10·5 will cover most of the examples likely to be encountered ; this permits of the use of thymol blue, thymolphthalein, or phenolphthalein.

Weak base and strong acid. The pH at the equivalence point is computed from the equation :

$$pH = 1/2\, pK_w - 1/2\, pK_b - 1/2 \log c.$$

The pH range for bases with $K_b > 10^{-5}$ is 3—7, and for weaker bases ($K_b > 10^{-6}$) 3—5. Suitable indicators will be methyl red, methyl orange, methyl yellow, bromo-cresol green, and bromo-phenol blue.

Weak acid and weak base. There is no sharp rise in the neutralisation curve and, generally, no simple indicator can be used. The titration should therefore be avoided, if possible. The approximate pH at the equivalence point can be computed from the equation :

$$pH = 1/2\, pK_w + 1/2\, pK_a - 1/2\, pK_b.$$

It is sometimes possible to employ a mixed indicator which exhibits a colour change over a very limited pH range, for example, neutral red—methylene blue for ammonia solution and acetic acid.

As a general rule, wherever an indicator does not give a sharp end point, it is advisable to prepare an equal volume of a comparison solution containing the same quantity of indicator and of the final products and other components of the titration as in the solution under test, and to titrate to the colour shade thus obtained.

THEORY OF PRECIPITATION AND COMPLEX-FORMATION PROCESSES

I, 39. Precipitation reactions.—The most important precipitation processes in volumetric analysis utilise silver nitrate as the reagent (argentimetric processes). Our discussion of the theory will therefore be confined to argentimetric processes ; the same principles can, of course, be applied to other precipitation reactions. Let us consider the changes in ionic concentration which occur during the titration of 100 ml. of 0·1N sodium chloride with 0·1N silver nitrate. The solubility product of silver chloride at the laboratory temperature is $1{\cdot}2 \times 10^{-10}$. The initial concentration of chloride ions, $[Cl^-]$, is 0·1 g. equivalent per litre, or

$p\text{Cl}^- = 1$ (see Section **I, 17**). When 50 ml. of $0{\cdot}1N$ silver nitrate have been added, 50 ml. of $0{\cdot}1N$ sodium chloride remain in a total volume of 150 ml. : thus $[\text{Cl}^-] = 50 \times 0{\cdot}1/150 = 3{\cdot}33 \times 10^{-2}$, or $p\text{Cl}^- = 1{\cdot}48$. With 90 ml. of silver nitrate solution, $[\text{Cl}^-] = 10 \times 0{\cdot}1/190 = 5{\cdot}3 \times 10^{-3}$, or $p\text{Cl}^- = 2{\cdot}28$.

$$\text{Now} \quad [\text{Ag}^+] \times [\text{Cl}^-] = 1{\cdot}2 \times 10^{-10} = S_{\text{AgCl}},$$
$$\text{or} \quad p\text{Ag}^+ + p\text{Cl}^- = 9{\cdot}92 = p\text{AgCl}.$$

In the last calculation, $p\text{Cl}^- = 1{\cdot}48$, hence $p\text{Ag}^+ = 9{\cdot}92 - 1{\cdot}48 = 8{\cdot}44$. In this manner, the various concentrations of chloride and silver ions can be computed up to the equivalence point. At the equivalence point :

$$\text{Ag}^+ = \text{Cl}^- = \sqrt{S_{\text{AgCl}}},$$
$$p\text{Ag}^+ = p\text{Cl}^- = 1/2\, p\text{AgCl} = 9{\cdot}92/2 = 4{\cdot}96,$$

and a saturated solution of silver chloride with no excess of silver or chloride ions is present.

With 100·1 ml. of silver nitrate solution, $[\text{Ag}^+] = 0{\cdot}1 \times 0{\cdot}1/200{\cdot}1 = 5 \times 10^{-5}$, or $p\text{Ag}^+ = 4{\cdot}30$; $p\text{Cl}^- = p\text{AgCl} - p\text{Ag}^+ = 9{\cdot}92 - 4{\cdot}30 = 5{\cdot}62$.*

The values computed in this way up to the addition of 110 ml. of $0{\cdot}1N$ silver nitrate are collected in Table XIV. Similar values for the titration of 100 ml. of $0{\cdot}1N$ potassium iodide with $0{\cdot}1N$ silver nitrate are included in the same Table ($S_{\text{AgI}} = 1{\cdot}7 \times 10^{-16}$).

It will be seen by inspecting the silver ion exponents in the neighbourhood of the equivalence point (say, between 99·8 and 100·2 ml.) that there is a marked change in the silver ion concentration, although the change is more pronounced for silver iodide than for the silver chloride since the solubility product of the latter is about 10^6 larger than for the former. This is shown more clearly in the titration curve in Fig. 1-12, which represents the changes of $p\text{Ag}^+$ in the range between 10 per cent before and 10 per cent after the stoichiometric point in the titration of $0{\cdot}1N$ chloride and $0{\cdot}1N$ iodide respectively with $0{\cdot}1N$ silver nitrate. An almost identical curve is obtained by potentiometric titration with the silver electrode see (Section **I, 52**) ; the $p\text{Ag}^+$ values may be computed from the e.m.f. figures exactly as in the calculation of $p\text{H}$.

*** This is not strictly true, since the dissolved silver chloride will contribute silver and chloride ions to the solution ; the actual concentration is *ca.* 1×10^{-5} g. ions per litre. If the excess of silver ions added is greater than 10 times this value, *i.e.*, $> 10\sqrt{S_{\text{AgCl}}}$, the error introduced by neglecting the ionic concentration produced by the dissolved salt may be taken as negligible for the purpose of the ensuing discussion.**

TABLE XIV. TITRATION OF 100 ML. OF 0·1N NaCl AND 100 ML. of 0·1N KI RESPECTIVELY WITH 0·1N $AgNO_3$ ($S_{AgCl} = 1{\cdot}2 \times 10^{-10}$; $S_{AgI} = 1{\cdot}7 \times 10^{-16}$)

Ml. of 0·1N $AgNO_3$ *added*	*Titration of Chloride*		*Titration of iodide*	
	pCl^-	pAg^+	pI^-	pAg^+
0	1·0	—	1·0	—
50	1·5	8·4	1·5	14·3
90	2·3	7·6	2·3	13·5
95	2·6	7·3	2·6	13·2
98	3·0	6·9	3·0	12·8
99	3·3	6·6	3·3	12·5
99·5	3·7	6·2	3·7	12·1
99·8	4·0	5·9	4·0	11·8
99·9	4·3	5·6	4·3	11·5
100·0	5·0	5·0	7·9	7·9
100·1	5·6	4·3	11·5	4·3
100·2	5·9	4·0	11·8	4·0
100·5	6·3	3·6	12·2	3·6
101	6·6	3·3	12·5	3·3
102	6·9	3·0	12·8	3·0
105	7·3	2·6	13·2	2·6
110	7·6	2·3	13·5	2·4

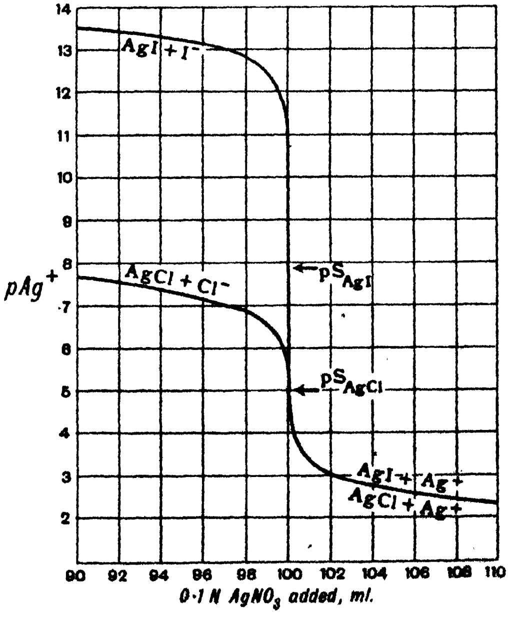

FIG. 1-12. Titration Curves of 100 ml. of 0·1N NaCl and of 100 ml. of 0·1N KI respectively with 0·1N $AgNO_3$ (Calculated).

I, 40. Complex formation reactions.—An example of this type of reaction is the titration of cyanide with silver nitrate solutions, a method first proposed by Liebig (1851). When a solution of silver nitrate is added to a solution containing cyanide ions (*e.g.*, an alkali cyanide) a white precipitate is formed when the two liquids first come into contact with one another, but on stirring it redissolves owing to the formation of a stable complex cyanide, the alkali salt of which is soluble :

$$AgNO_3 + 2KCN \rightleftharpoons K[Ag(CN)_2] + KNO_3,$$

or

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-.$$

When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver argento-cyanide (often termed silver cyanide) :

$$Ag^+ + [Ag(CN)_2]^- \rightarrow Ag[Ag(CN)_2].$$

The end point of the reaction is therefore indicated by the formation of a permanent precipitate or turbidity.

Let us attempt to investigate the suitability of this reaction for quantitative work and to calculate the titration error involved. The instability constant (Section **I, 12** ; Table V), *i.e.*,

$$[Ag^+] \times [CN^-]^2 / [\{Ag(CN)_2\}^-],$$

is $1{\cdot}0 \times 10^{-21}$ at the ordinary temperature. Let us suppose, for purposes of illustration, that an amount of potassium cyanide solution equivalent to 10 ml. of $0{\cdot}1N$ silver nitrate is employed, and that the volume at the end point is 100 ml. The concentration of the complex $K[Ag(CN)_2]$ will then be 0·01 molar. Here the Ag^+ and CN^- ions present will be derived from the dissociation of the complex $[Ag(CN)_2]^-$ ion. At the stoichiometric point :

$$[CN^-] = 2[Ag^+] = 2x,$$

hence $$\frac{[Ag^+] \times [CN^-]^2}{[\{Ag(CN)_2\}^-]} = 1{\cdot}0 \times 10^{-21} = \frac{x \times (2x)^2}{0{\cdot}01},$$

or $$x = \sqrt[3]{2{\cdot}5 \times 10^{-24}} = 1{\cdot}36 \times 10^{-8},$$

or $$[Ag^+] = 1{\cdot}36 \times 10^{-8}, \text{ and } [CN^-] = 2{\cdot}72 \times 10^{-8}.$$

The solubility product of silver argentocyanide, $[Ag^+] \times [\{Ag(CN)_2\}^-]$, is $2{\cdot}25 \times 10^{-12}$, hence precipitation of this substance will commence when :

$$[Ag^+] > \frac{2{\cdot}25 \times 10^{-12}}{[\{Ag(CN)_2\}^-]} > \frac{2{\cdot}25 \times 10^{-12}}{0{\cdot}01} > 2{\cdot}25 \times 10^{-10}.$$

The silver ion concentration at the theoretical end point is $1{\cdot}36 \times 10^{-8}$, hence precipitation will occur just before this. The difference is so small, however, that for all practical purposes the titration error is negligible ; moreover, in practice, the theoretical end point will be exceeded in order to produce enough precipitate to be visible.

The above method yields satisfactory results if the reagent is added very slowly near the end point, but is not applicable to ammoniacal solutions owing to the removal of the silver ions by the formation of the soluble complex $[Ag(NH_3)_2]^+$ (see Section **I, 12**). An alternative procedure is to work in ammoniacal solution in the presence of a little alkali iodide (G. Dénigès, 1895) : the end point is marked by the formation of a turbidity of silver iodide (see Sections **I, 11, 12**).

I, 41. Determination of end points in precipitation and in complex formation reactions.—Many methods are utilised in determining end points in these reactions, but only the most important will be mentioned here.

A. Formation of a coloured precipitate. This may be illustrated by the Mohr procedure (1856) for the determination of chloride and bromide. In the titration of a neutral solution of, say, choride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red silver chromate.

The theory of the process is as follows. We have here a case of fractional precipitation (Section **I, 11**), the two sparingly soluble salts being silver chloride (S.P. $1{\cdot}2 \times 10^{-10}$) and silver chromate (S.P. $1{\cdot}7 \times 10^{-12}$). Let us consider an actual example encountered in practice, *viz.*, the titration of, say, $0{\cdot}1N$ silver nitrate with $0{\cdot}1N$ sodium chloride in the presence of a few ml. of dilute potassium chromate solution. Silver chloride is the less soluble salt and, furthermore, the initial chloride concentration is high, hence silver chloride will be precipitated. At the first point where red silver chromate is just precipitated, we shall have both salts in equilibrium with the solution, hence :

$$[Ag^+] \times [Cl^-] = S_{AgCl} = 1{\cdot}2 \times 10^{-10} ;$$

$$[Ag^+]^2 \times [CrO_4^{--}] = S_{Ag_2CrO_4} = 1{\cdot}7 \times 10^{-12} ;$$

$$[Ag^+] = \frac{S_{AgCl}}{[Cl^-]} = \sqrt{\frac{S_{Ag_2CrO_4}}{[CrO_4^{--}]}} ;$$

$$\frac{[Cl^-]}{\sqrt{[CrO_4^{--}]}} = \frac{S_{AgCl}}{\sqrt{S_{Ag_2CrO_4}}} = \frac{1{\cdot}2 \times 10^{-10}}{\sqrt{1{\cdot}7 \times 10^{-12}}} = 9{\cdot}2 \times 10^{-5}$$

At the equivalence point $[Cl^-] = \sqrt{S_{AgCl}} = 1{\cdot}1 \times 10^{-5}$. If silver chromate is to precipitate at this chloride ion concentration :

$$[CrO_4^{--}] = \left(\frac{[Cl^-]}{9{\cdot}2 \times 10^{-5}}\right)^2 = \left(\frac{1{\cdot}1 \times 10^{-5}}{9{\cdot}2 \times 10^{-5}}\right)^2 = 1{\cdot}4 \times 10^{-2}$$

or the potassium chromate solution should be 0·014 molar. It should be noted that a slight excess of silver nitrate solution must be added before the red colour of silver chromate is visible. In practice, a more dilute solution (0·002—0·004 molar) of potassium chromate is generally used, since a chromate solution of concentration 0·01—0·02 molar imparts a distinct deep orange colour to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. We can readily calculate the error thereby introduced, for if $[CrO_4^{--}]$ = (say) 0·003, silver chromate will be precipitated when :

$$[Ag^+] = \sqrt{\frac{S_{Ag_2CrO_4}}{CrO_4^{--}}} = \sqrt{\frac{1{\cdot}7 \times 10^{-12}}{3 \times 10^{-3}}} = 2{\cdot}4 \times 10^{-5}.$$

If the theoretical concentration of indicator is used :

$$[Ag^+] = \sqrt{\frac{1{\cdot}7 \times 10^{-12}}{1{\cdot}4 \times 10^{-2}}} = 1{\cdot}1 \times 10^{-5}.$$

The difference is $1{\cdot}3 \times 10^{-5}$ g. equivalent per litre. If the volume of the solution at the equivalent point is 150 ml., then this corresponds to $1{\cdot}3 \times 10^{-5} \times 150 \times 10^4 / 1000 =$ 0·02 ml. of 0·1*N* silver nitrate. This is the theoretical titration error, and is therefore negligible. In actual practice another factor must be considered, *viz.*, the small excess of silver nitrate solution which must be added before the eye can detect the colour change in the solution ; this is of the order of one drop or *ca.* 0·05 ml. of 0·1*N* silver nitrate.

The titration error will increase with increasing dilution of the solution being titrated and is quite appreciable (*ca.* 0·6 per cent) in dilute, say, 0·01*N*, solutions when the chromate concentration is of the order 0·002—0·004 molar. This is most simply allowed for by means of an indicator blank determination, *e.g.*, by measuring the volume of standard silver nitrate solution required to give a perceptible colouration when added to distilled water containing the same quantity of indicator as is employed in the titration. This volume is subtracted from the volume of standard solution used.

It must be mentioned that the titration should be carried out in neutral solution or in very faintly alkaline solution, *i.e.*, within the *p*H range 6·5 to 9. In acid solution, the following reaction occurs:

$$2CrO_4^{--} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{--} + H_2O.$$

$HCrO_4^-$ is a weak acid, consequently the chromate ion concentration is reduced and the solubility product of silver chromate may not be exceeded. In markedly alkaline solutions, silver hydroxide (S.P. $2{\cdot}3 \times 10^{-8}$) might be precipitated. A simple method of making an acid solution neutral is to add an excess of pure calcium carbonate.

B. Formation of a soluble coloured compound. This procedure is exemplified by the method of Volhard (1878) for the titration of silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first a precipitate of silver thiocyanate (S.P. $7{\cdot}1 \times 10^{-13}$):

$$Ag^+ + CNS^- \rightleftharpoons AgCNS.$$

When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown colouration, due to the formation of the complex ferri-thiocyanate ion.*

$$Fe^{+++} + 6CNS^- \rightleftharpoons [Fe(CNS)_6]^{---}$$

$$(or \quad 2Fe^{+++} + 6CNS^- \rightleftharpoons Fe[Fe(CNS)_6] \rightleftharpoons Fe^{+++} + [Fe(CNS)_6]^{---}).$$

This method may be applied to the determination of chlorides, bromides and iodides in acid solution. Excess of standard silver nitrate solution is added and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

$$Ag^+ + Cl^- \rightleftharpoons AgCl;$$
$$Ag^+ + CNS^- \rightleftharpoons AgCNS.$$

The two sparingly soluble salts will be in equilibrium with the solution, hence:

$$\frac{[Cl^-]}{[CNS^-]} = \frac{S_{AgCl}}{S_{AgCNS}} = \frac{1{\cdot}2 \times 10^{-10}}{7{\cdot}1 \times 10^{-13}} = 170.$$

---

* According to Bent and French [1941] the colouration is due to the $FeCNS^{++}$ ion:

$$Fe^{+++} + CNS^- \rightleftharpoons FeCNS^{++}.$$

When the excess of silver has reacted, the excess of thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble salt until the ratio $[Cl^-]/[CNS^-]$ in the solution is 170 :

$$AgCl + CNS^- \rightleftharpoons AgCNS + Cl^-.$$

This will take place before reaction occurs with the ferric ions in the solution, and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable : (i) the silver chloride is filtered off, and the filtrate and washings are titrated ; (ii) the silver chloride is coagulated, and thus rendered less reactive by boiling, and the mixture is cooled and titrated ; (iii) the addition of a few ml. of ether or, preferably, of 1 ml. of nitrobenzene, which causes coagulation, before back titration.

With bromides, we have the equilibrium :

$$\frac{[Br^-]}{[CNS^-]} = \frac{S_{AgBr}}{S_{AgCNS}} = \frac{3{\cdot}5 \times 10^{-13}}{7{\cdot}1 \times 10^{-13}} = 0{\cdot}5.$$

The titration error is small and no difficulties arise in the determination of the end point. Silver iodide (S.P. $1{\cdot}7 \times 10^{-16}$) is less soluble than the bromide ; the titration error is negligible, but the ferric iron indicator should not be added until excess of silver is present since the dissolved iodide reacts with the ferric iron :

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2.$$

C. Use of adsorption indicators. K. Fajans (1923-1924) has introduced a new type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and during the process of adsorption a change occurs in the indicator which leads to a substance of different colour ; they have therefore been termed **adsorption indicators.** The substances employed are either acid dyes such as those of the fluorescein series, *e.g.*, fluorescein and eosin which are utilised as the sodium salts, or basic dyes, such as those of the rhodamine series (*e.g.*, rhodamine 6G), which are applied as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids (see Section **I, 56**). When silver nitrate solution is titrated with a solution of a chloride, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions) ; this may be termed the primarily adsorbed layer, and it will hold by secondary adsorption oppositely charged ion present in solution (shown diagrammatically in Fig. 1-13*a*). As soon as the stoichiometric point is reached, silver ions are present in excess ; these will now be primarily adsorbed and nitrate ions will be held by secondary adsorption (Fig. 1-13 *b*). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than the nitrate ion, is immediately adsorbed, and will reveal its presence in the precipitate, not by its own colour, which is that of the solution, but by the formation of the red (or pink) silver fluoresceinate on the surface with first trace of excess of silver ions.

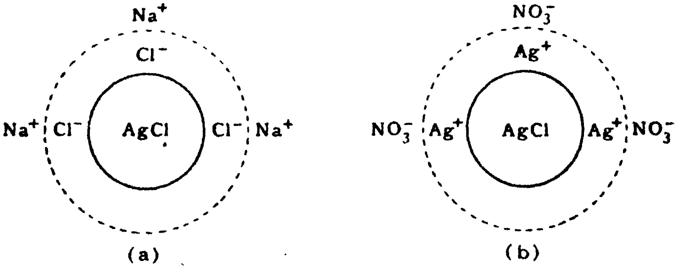

FIG. 1-13. (*a*) AgCl precipitated in the presence of excess of Cl^-.
(*b*) AgCl precipitated in the presence of excess of Ag^+.

An alternative view is that during the adsorption of the fluorescein ion a re-arrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the surface of the precipitate. If chloride is now added, the suspension will remain pink until chloride ions are present in excess, the adsorbed silver will then be converted into silver chloride, which will then primarily adsorb chloride ions. The fluorescein ions secondarily adsorbed will pass back into solution, to which they impart a greenish-yellow colour.

The following conditions will govern the choice of a suitable indicator :

(i) The precipitate should separate as far as possible in the colloidal condition. Large quantities of neutral salts, particularly of polyvalent ions, should be avoided owing to their coagulating effect. The solution should not be too dilute as the amount of precipitate formed will be small and the colcur change far from sharp with certain indicators.

(ii) The indicator ion must be of opposite charge to the ion of the precipitating agent.

(iii) The indicator ion should not be adsorbed before the particular compound has been completely precipitated, but it should be strongly adsorbed immediately after the equivalence point. The indicator ion should not be too strongly adsorbed by the precipitate; if this occurs, the adsorption of the indicator ion may be a primary process and will take place before the equivalence point, *e.g.*, eosin (tetrabromofluorescein) in the chloride-silver titration.

For the titration of chlorides, fluorescein may be used. This indicator is a weak acid ($K_a = ca.\ 1 \times 10^{-8}$) and cannot be employed in strongly acid solutions. Titration should be carried out in neutral or in feebly acid (acetic acid) solutions ; acid solutions may be treated with a slight excess of sodium acetate. Alternatively, dichlorofluorescein, which is a stronger acid, may be utilised in slightly acid solutions ($p\text{H} > 4{\cdot}4$) ; this indicator has a further advantage in that it is applicable in very dilute solutions.

For the titration of bromides, iodides and thiocyanates with silver, eosin is a suitable indicator ; the colour on the precipitate is magenta. The best results for iodides are obtained with dimethyldi-iodofluorescein, which gives a blue-red colour on the precipitate. The titration of silver solutions with bromide as the precipitating agent is best effected with rhodamine 6G, the precipitate assuming a violet colour at the end point ; a sharp end point is obtained with this indicator in the presence of nitric acid up to a concentration of 2*N*. Cyanides may be titrated with standard silver solutions using diphenylcarbazide as the adsorption indicator (see Section **I, 41**) ; the precipitate is pale-violet at the end point.

D. Turbidity method. The appearance of a turbidity is sometimes utilised to mark the end point of a reaction, as in Liebig's method for cyanides (see Section **I, 41**). A method which should be included here is the **equal turbidity procedure** introduced by Gay Lussac (1832) for the determination of silver with chloride. At the end point of the titration of, say, sodium chloride with silver nitrate solution, a solution of sodium nitrate which is saturated with silver chloride is obtained. If the clear supernatant liquid is withdrawn, and equal volumes treated with equivalent strengths of silver nitrate and sodium chloride solutions respectively, then equal turbidities of silver chloride should be produced. If equal turbidities are not found, the titration is continued with sodium chloride or silver nitrate to the point of equal turbidities.

This method yields very accurate results in experienced hands, and is still employed for the determination of silver in alloys in the mints of certain governments. For ordinary work, however, any of the methods described above will be found more suitable for the average student. It must, however, be pointed out that nephelometric methods are employed in atomic weight determinations and, indeed, owe their introduction to T. W. Richards who first used a simple, but effective, nephelometer in connexion with his researches on the atomic weight of silver (compare Section **V, 5**).

I, 42. THEORY OF OXIDATION—REDUCTION REACTIONS

Reference has already been made in Section **I, 23** to the fact that oxidation may be defined as the loss of electrons, and reduction as the gain of electrons by an atom or group of combined atoms. Thus in the reduction of ferric chloride by stannous chloride:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

or $$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++};$$

for every gram atom of ferric iron (56 g.) reduced 96,500 coulombs or one Faraday of electricity is lost by the iron, and for every gram atom of stannous tin (119 g.) oxidised, the latter gains 2 × 96,500 coulombs or two Faradays.*

According to modern theory, an electric current is essentially a transfer of electrons. It should therefore be possible to obtain direct proof of the transfer of electricity in the oxidation-reduction reaction under suitable experimental conditions. This may be shown by the following experiment

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* It follows from Faraday's laws (Section **I, 64**) that each gram equivalent weight of an ion is associated with a charge of one Faraday of electricity. A change of charge of one thus corresponds to the gain or loss of one Faraday per formula weight of the substance.

(Fig. 1-14). Solutions of stannous chloride and of ferric chloride, each acidified with dilute hydrochloric acid in order to increase the conductivity, are placed in separate beakers **A** and **B**, and the two solutions are connected by means of a " salt bridge" containing sodium chloride. The latter consists of a U-tube filled with a solution of a conducting electrolyte, such as sodium chloride, and stoppered at each end with a plug of cotton wool in order to minimise diffusion. It connects the two parts of the redox system, and prevents mixing. The electrolyte in solution in the salt bridge is always selected so that it does not react chemically with either of the solutions which it connects. Platinum foil electrodes are introduced into each of the solutions, and the two electrodes are connected to a milli-voltmeter **V**. When the circuit is closed, it will be found that the current in the external circuit passes from the stannous chloride solution to the ferric chloride solution. After a time, stannic ions can be detected in **A** and ferrous ions in **B**.

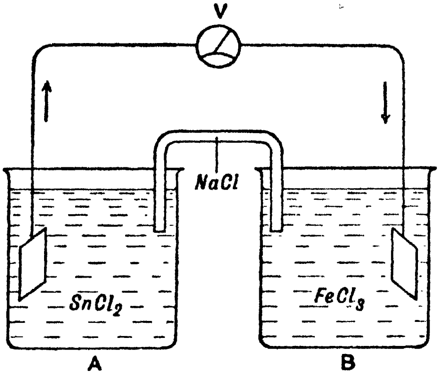

FIG. 1-14.

In the preceding experiment the flow of current is due to the e.m.f. produced by the chemical change in the redox reaction. It can also be shown that an electric current, say from a storage battery, will give rise to oxidation-reduction reactions. Thus, if in Fig. 1–14 beaker **A** contains ferrous ammonium sulphate acidified with dilute sulphuric acid, and beaker **B** ferric chloride likewise acidified with dilute sulphuric acid, the salt bridge dilute sulphuric acid, and the millivoltmeter **V** replaced by a 6-volt battery, then after some time ferric ions can be detected in **A** and ferrous ions in **B**.

It is a well-known fact that oxidants and reductants vary considerably in strength. Information of a qualitative character as to the relative strengths (compare relative strengths of weak acids and bases as expressed by their dissociation constants in Table II) would be of considerable practical value. A method which suggests itself at once is the measurement of the e.m.f. of redox reactions under standard conditions. This is indeed the method which is employed, but before this can be understood by the student, it will be necessary to consider the subject of electrode potentials.

I, 43. Electrode potentials.—When a metal is immersed in a solution containing its own ions, say, zinc in zinc sulphate solution, a potential difference E is established between the metal and the solution. The potential difference E for an electrode reaction, $M \rightleftharpoons M^{n+} + n\epsilon$, is given by the expression* :

$$E = \frac{RT}{nF} \log_e a_+ + E_o \qquad \text{(i)},$$

where R is the gas constant, T is the absolute temperature, F the Faraday, n the valency of the ions, a_+ the activity of the ions in the solution, and E_o is a constant dependent upon the metal. Equation (i) can be simplified by introducing the known values of R and F, and converting the natural logarithms to base 10 by multiplying by 2·3026 ; it then becomes :

$$E = \frac{0{\cdot}0001982T}{n} \log a_+ + E_o \qquad \text{(ii)}.$$

For a temperature of 25°C ($T = 298°$) :

$$E = \frac{0{\cdot}0591}{n} \log a_+ + E_o \qquad \text{(iii)}.$$

For most purposes in quantitative analysis, it is sufficiently accurate to substitute a_+ by $c_i{}^+$, the ion concentration (in mols per litre) :

$$E = \frac{0{\cdot}0591}{n} \log c_{i+} + E_o \qquad \text{(iv)}.$$

The latter is often known as the Nernst equation.

For a non-metal, which yields negative ions, equation (iii) becomes :

$$E = E_o - \frac{0{\cdot}0591}{n} \log a_- \qquad \text{(v)},$$

where a_- is the activity of the negative ions. Here also, we may introduce the approximation of substituting c_{i-} for a_-.

If in equation (iv), c_{i+} is put equal to unity, E is equal to E_o. E_o is called the **standard or normal potential of the metal.**

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* For a derivation of this equation, see any good text book of physical chemistry, or the author's *Text Book of Qualitative Chemical Analysis*, 1937, p. 67. (Longmans Green and Co. Ltd.).

In order to determine the potential difference between an electrode and a solution, it is necessary to have another electrode and a solution, the potential difference between which is known. The two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be directly measured. The e.m.f. of the cell is the arithmetical sum or difference of the electrode potentials (depending upon the sign of these two potentials) ; the value of the unknown potential can then be calculated. In practice the standard electrode potential used for comparative purposes is the **molar or normal hydrogen electrode.** This consists of a piece of platinum foil, coated with platinum black by an electrolytic process, and immersed in a solution of hydrochloric acid, normal with respect to hydrogen ions (more correctly, in a solution of hydrochloric acid containing hydrogen ions of unit activity). Hydrogen gas at a pressure of one atmosphere is passed over the foil through the side tube **C** (Fig. 1-15) and escapes through the small openings **B** in the surrounding glass tube **A** ; the foil is thus kept saturated with the gas. Connection between the platinum foil sealed into the tube **D** with an outer circuit is made with mercury in **D**. The platinum black has the remarkable property of adsorbing large quantities of hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance ; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode. Under fixed conditions, *viz.*, of atmospheric pressure and normal concentration of hydrogen ions in the solution in contact with the electrode, the hydrogen electrode possesses a definite potential at all temperatures. By connecting the normal hydrogen electrode with a metal electrode (a metal in contact with a molar solution of its ions) by means of a salt (say, potassium chloride) bridge, the **normal, molar,** or **standard electrode potential** may be determined. Other electrodes, particularly the calomel electrode and the silver-silver chloride electrode, the potentials of which have been determined

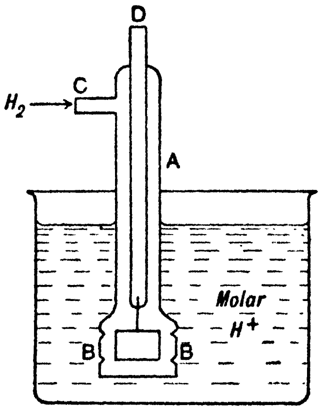

FIG. 1-15.

by direct reference to the normal hydrogen electrode, are often used in practice owing to convenience of manipulation. The former is discussed in Section **I, 52,** but for a fuller treatment the student is referred to text books of electrochemistry.*

We may therefore define the **standard** or **normal electrode potential** of an element as the e.m.f. produced when a half cell consisting of the element immersed in a molar solution of its ions (more correctly, in a solution of its ions possessing unit activity) is coupled with a molar hydrogen electrode, the potential of which is assumed equal to zero. The more important standard electrode potentials at 25°C are collected in Table XV; the sign of the potential here adopted is that of the charge on the electrode.

TABLE XV. STANDARD ELECTRODE POTENTIALS AT 25° C.

Li/Li^+	$-2{\cdot}959$	Co/Co^{++}	$-0{\cdot}28$
K/K^+	$-2{\cdot}924$	Ni/Ni^{++}	$-0{\cdot}23$
Ca/Ca^{++}	$-2{\cdot}76$	Sn/Sn^{++}	$-0{\cdot}136$
Na/Na^+	$-2{\cdot}715$	Pb/Pb^{++}	$-0{\cdot}122$
Mg/Mg^{++}	$-1{\cdot}55$	$Pt(H_2)/H^+$	$0{\cdot}000$
Al/Al^{+++}	$-1{\cdot}33$	Bi/Bi^{+++}	$+0{\cdot}226$
Mn/Mn^{++}	$-1{\cdot}1$	Cu/Cu^{++}	$+0{\cdot}344$
Zn/Zn^{++}	$-0{\cdot}762$	Hg/Hg_2^{++}	$+0{\cdot}799$
Cr/Cr^{++}	$-0{\cdot}557$	Ag/Ag^+	$+0{\cdot}798$
Fe/Fe^{++}	$-0{\cdot}441$	Pd/Pd^{++}	$+0{\cdot}82$
Cd/Cd^{++}	$-0{\cdot}401$	Au/Au^{+++}	$+1{\cdot}36$

When metals are arranged in the order of their standard electrode potentials, the so-called **electrochemical series** of the metals is obtained. The greater the negative value of the potential, the greater is the tendency of the metal to pass into the ionic state. A metal with a more negative potential will displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminium, zinc or iron will displace copper from solutions of its salts; lead will displace copper, mercury or silver; copper will displace silver.

The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent; the more negative the element. the more powerful is its action as a reductant.

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* See, for example, S. Glasstone, *The Electrochemistry of Solutions* (1937).

I, 44. Concentration cells.—The electrode potential varies with the concentration of the ions in the solution. Hence by bringing two electrodes of the same metal, but immersed in solutions containing different concentrations of the ions into contact, a cell may be formed. Such a cell is termed a **concentration cell.** The e.m.f. of the cell will be the algebraic difference of the two potentials, if a salt bridge be inserted to eliminate the liquid-liquid junction potential. It may be calculated as follows. At 25°C :

$$
\begin{aligned}
E &= \frac{0{\cdot}0591}{n}\log c_1 + E_o - \frac{0{\cdot}0591}{n}\log c_2 + E_o,\\
&= \frac{0{\cdot}0591}{n\cdot}\log\frac{c_1}{c_2}\text{ , where } c_1 > c_2.
\end{aligned}
$$

As an example we may consider the cell :

$$
\text{Ag}\ \underset{\underset{E_2}{\leftarrow}}{\overset{-}{\Big|}}\ \begin{matrix}\text{AgNO}_3\text{ aq.}\\ [\text{Ag}^+] = 0{\cdot}00475M\end{matrix}\ \Big\|\ \begin{matrix}\text{AgNO}_3\text{ aq.}\\ [\text{Ag}^+] = 0{\cdot}043M\end{matrix}\ \underset{\underset{E_1}{\rightarrow}}{\overset{+}{\Big|}}\ \text{Ag.}
$$

Assuming that there is no potential difference at the liquid junction :

$$
E = E_1 - E_2 = \frac{0{\cdot}0591}{1}\log\frac{0{\cdot}043}{0{\cdot}00475} = \mathit{0{\cdot}056\ volt.}
$$

I, 45. Calculation of the e.m.f. of a voltaic cell.—An interesting application of electrode potentials is to the calculation of the e.m.f. of a voltaic cell. One of the simplest of galvanic cells is the Daniell cell. It consists of a rod of zinc dipping into zinc sulphate solution and a strip of copper in copper sulphate solution ; the two solutions are generally separated by placing one inside a porous pot and the other in the surrounding vessel. The cell may be represented as :

$$\text{Zn}\,|\,\text{ZnSO}_4\text{ aq.}\,\|\,\text{CuSO}_4\text{ aq.}\,|\,\text{Cu.}$$

At the zinc electrode, zinc ions pass into solution leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode, rendering it positively charged. By completing the external circuit, the current (electrons) passes from the zinc to the copper. The chemical reactions in the cell are as follows :

(*a*) zinc electrode— $\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2\epsilon$;
(*b*) copper electrode— $\text{Cu}^{++} \rightleftharpoons \text{Cu} - 2\epsilon$.

The net chemical reaction is :

$$Zn + Cu^{++} = Zn^{++} + Cu.$$

The potential difference at each electrode may be calculated by the formula given above, and the e.m.f. of the cell is the algebraic difference of the two potentials, the correct sign being applied to each.

As an example we may calculate the e.m.f. of the Daniell cell with molar concentrations of zinc ions and cupric ions.

$$E = E_{o(\mathrm{Cu})} - E_{o(\mathrm{Zn})} = +0{\cdot}34 - (-0{\cdot}76) = \mathit{1{\cdot}10\ volts}.$$

The small potential difference produced at the contact between the two solutions (the so-called liquid-junction potential) is neglected.

I, 46. Oxidation reduction cells.—Reduction is accompanied by a gain of electrons and oxidation by a loss of electrons. In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and electrons. If an inert electrode, such as platinum, is placed in a redox system, for example one containing ferric and ferrous ions, it will assume a definite potential indicative of the position of equilibrium. If the oxidation tendency predominates, the system will take electrons from the platinum, leaving the latter positively charged ; if, however, the system has reducing properties, electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing properties of the system.

To obtain comparative values of the " strengths " of oxidising agents, it is necessary, as in the case of the electrode potentials of the metals, to measure under standard experimental conditions the potential difference between the platinum and the solution relative to a standard of reference. The primary standard is the molar or normal hydrogen electrode (Section **I, 43**), and its potential is taken as zero. The standard experimental conditions for the redox system are those in which the ratio of the concentration of the oxidant to that of the reductant is unity. Thus for a ferrous-ferric chloride electrode, the redox cell would be :

$$\mathrm{Pt} \;\Big|\; \begin{matrix}\mathrm{Fe^{+++}} \\ \mathrm{Fe^{++}}\end{matrix} \;\Big\|\; \mathrm{H^{+}} \;\Big|\; \mathrm{H_2\,(Pt)}.$$

The potential measured in this way is called the **standard oxidation potential.** A selection of these is given in Table XVI. The sign of the potential is that of the electrode.

TABLE XVI. STANDARD OXIDATION POTENTIALS AT 25°C.

Electrode	*Electrode Reaction*	$E°$ (*volts*)
Co^{+++}, Co^{++} / Pt*	$Co^{+++} + \epsilon \rightleftharpoons Co^{++}$	+ 1·82
Pb^{++++}, Pb^{++} / Pt	$Pb^{++++} + 2\epsilon \rightleftharpoons Pb^{++}$	+ 1·75
MnO_4^-, Mn^{++} / Pt	$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O$	+ 1·52
Ce^{++++}, Ce^{+++} / Pt	$Ce^{++++} + \epsilon \rightleftharpoons Ce^{+++}$	+ 1·45
ClO_3^-, Cl^- / Pt	$ClO_3^- + 6H^+ + 6\epsilon \rightleftharpoons Cl^- + 3H_2O$	+ 1·45
BrO_3^-, Br^- / Pt	$BrO_3^- + 6H^+ + 6\epsilon \rightleftharpoons Br^- + 3H_2O$	+ 1·42
Cl_2, $2Cl^-$ /Pt	$Cl_2 + 2\epsilon \rightleftharpoons 2Cl^-$	+ 1·36
$Cr_2O_7^{--}$, $2Cr^{+++}$ / Pt	$Cr_2O_7^{--} + 14H^+ + 6\epsilon \rightleftharpoons 2Cr^{+++} + 7H_2O$	+ 1·3
IO_3^-, I^- / Pt	$IO_3^- + 6H^+ + 6\epsilon \rightleftharpoons I^- + 3H_2O$	+ 1·2
Br_2, $2Br^-$ / Pt	$Br_2 + 2\epsilon \rightleftharpoons Br^-$	+ 1·07
Fe^{+++}, Fe^{++} / Pt	$Fe^{+++} + \epsilon \rightleftharpoons Fe^{++}$	+ 0·75
H_3AsO_4, H_3AsO_3 / Pt	$H_3AsO_4 + 2H^+ + 2\epsilon \rightleftharpoons H_3AsO_3 + H_2O$	+ 0·57
I_2, $2I^-$ / Pt	$I_2 + 2\epsilon \rightleftharpoons 2I^-$	+ 0·54
$Fe(CN)_6^{---}$ $Fe(CN)_6^{----}$ / Pt	$Fe(CN)_6^{---} + \epsilon \rightleftharpoons Fe(CN)_6^{----}$	+ 0·49
UO_2^{++}, U^{++++} / Pt	$UO_2^{++} + 4H^+ + 2\epsilon \rightleftharpoons U^{++++} + 2H_2O$	+ 0·36
Cu^{++}, Cu^+ / Pt	$Cu^{++} + \epsilon \rightleftharpoons Cu^+$	+ 0·16
Sn^{++++}, Sn^{++} / Pt	$Sn^{++++} + 2\epsilon \rightleftharpoons Sn^{++}$	+ 0·14
Ti^{++++}, Ti^{+++} / Pt	$Ti^{++++} + \epsilon \rightleftharpoons Ti^{+++}$	+ 0·04
H_2, $2H^+$ / Pt	$2H^+ + 2\epsilon \rightleftharpoons H_2$	0·00
Cr^{+++}, Cr^{++} / Pt	$Cr^{+++} + \epsilon \rightleftharpoons Cr^{++}$	− 0·4
$S°$, S^{--} / Pt	$S° + 2\epsilon \rightleftharpoons S^{--}$	− 0·55

The oxidation potentials enable us to predict which ions will oxidise or reduce other ions at molar concentrations. The most powerful oxidising agents are those at the upper end of the Table, and the most powerful reducing agents at the lower end. Thus permanganate ions can oxidise Cl^-, Br^-, I^-, Fe^{++} and $Fe(CN)_6^{----}$; ferric ions can oxidise H_3AsO_3 and I^-, but not $Cr_2O_7^{--}$ or Cl^- ions. It must be emphasised that oxidation potentials do not give any information as to the speed of the reaction ; in some cases, as in the oxidation of arsenious acid by ceric ions, the presence of a catalyst is necessary in order that the reaction may proceed with reasonable velocity.

I, 47. Calculation of the oxidation potential.—A reversible oxidation-reduction reaction may be written in the form (*oxidant* = substance in oxidised state, *reductant* = substance in reduced state) :

$$\underbrace{\text{Reductant}}_{\textit{Red}} \rightleftharpoons \underbrace{\text{Oxidant}}_{\textit{Ox}} + n\epsilon.$$

---

* The symbol Pt throughout this Table must be interpreted as any inert, unattackable electrode.

The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression :

$$E_T = E^\circ + \frac{RT}{nF} \log_e \frac{a_{Ox}}{a_{Red}} \qquad \text{(i)},$$

where E_T is the observed potential of the redox electrode at T°, E° is the standard oxidising potential, n the number of electrons gained by the oxidant in being converted into the reductant, and a_{Ox} and a_{Red} are the activities of the oxidant and reductant respectively.

Since activities are often difficult to determine directly, they may be replaced by concentrations ; the error thereby introduced is usually of no great importance. The equation therefore becomes :

$$E_T = E^\circ + \frac{RT}{nF} \log_e \frac{c_{Ox}}{c_{Red}} \quad . \quad \text{(i')}.$$

Substituting the known values of R and F, and changing from natural to common logarithms (by multiplying by 2·3026), we have for a temperature of 25°C (T = 288°) :

$$E_{25^\circ} = E^\circ + \frac{0{\cdot}0591}{n} \log \frac{[Ox]}{[Red]} \qquad \text{(i'')}.$$

If the concentrations (or, more accurately, the activities) of the oxidant and reductant are equal, $E_{25^\circ} = E^\circ$, *i.e.*, the standard oxidation potential. It follows from this expression that, for example, a ten-fold change in the ratio of the concentrations of the oxidant to the reductant will produce a change in the potential of the system of $0{\cdot}0591/n$ volts.

I, 48. Equilibrium constants of oxidation-reduction reactions.—The general equation for an oxidation-reduction electrode may be written :

$$pA + qB + rC + \ldots\ldots N\epsilon \rightleftharpoons sX + tY + uZ + \ldots\ldots$$

The potential is given by :

$$E = E^\circ + \frac{RT}{nF} \log_e \frac{a_X^s \cdot a_Y^t \cdot a_Z^u \ldots\ldots}{a_A^p \cdot a_B^q \cdot a_C^r \ldots\ldots},$$

where a refers to activities, and n to the number of electrons involved in the oxidation-reduction reaction. This expression reduces to the following for a temperature of 25°C (concentrations are substituted for activities in order to permit of its facile application in practice) :

$$E = E^\circ + \frac{0{\cdot}0591}{n} \log \frac{c_X^s \, . \, c_Y^t \, . \, c_Z^u \, \ldots\ldots}{c_A^p \, . \, c_B^q \, . \, c_C^r \, \ldots\ldots}.$$

It is, of course, possible to calculate the influence of the change of concentration of certain constituents of the system by the use of the latter equation. Consider, for example, the permanganate reaction :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O.$$

$$E = E^\circ + \frac{0{\cdot}0591}{5} \log \frac{[MnO_4^-] \times [H^+]^{8*}}{[Mn^{++}]} \quad \text{(at 25°C)}.$$

The concentration (or activity) of the water is taken as constant, since it is assumed that the reaction takes place in dilute solution, and the concentration of the water does not change appreciably as the result of the reaction. The equation may be written in the form :

$$E = E^\circ + \frac{0{\cdot}0591}{5} \log \frac{[MnO_4^-]}{[Mn^{++}]} + \frac{0{\cdot}0591}{5} \log [H^+]^8.$$

This enables us to calculate the effect of change in the ratio $[MnO_4^-] / [Mn^{++}]$ at constant hydrogen ion concentration, other factors being maintained constant. In this particular case difficulties are experienced in the latter calculation owing to the fact that the reduction products of the permanganate ion vary at different hydrogen ion concentrations. In other cases no such difficulties arise, and the calculation may be employed with confidence. Thus in the reaction :

$$H_3AsO_4 + 2H^+ + 2\epsilon \rightleftharpoons H_3AsO_3 + H_2O,$$

$$E = E^\circ + \frac{0{\cdot}0591}{2} \log \frac{[H_3AsO_4] \times [H^+]^2}{[H_3AsO_3]} \quad \text{(at 25°C)},$$

or $$E = E^\circ + \frac{0{\cdot}0591}{2} \log \frac{[H_3AsO_4]}{[H_3AsO_3]} + \frac{0{\cdot}0591}{2} \log [H^+]^2.$$

We are now in a position to calculate the equilibrium constants of oxidation-reduction reactions, and thus to determine whether such reactions can find application in quantitative analysis. Let us consider first the simple reaction :

---

* More accurately, activities should be employed. The square brackets denote molecular concentrations.

$$Cl_2 + 2Fe^{++} \rightleftharpoons 2Cl^- + 2Fe^{+++}.$$

The equilibrium constant is given by :

$$\frac{[Cl^-]^2 \times [Fe^{+++}]^2}{[Cl_2] \times [Fe^{++}]^2} = K.$$

The reaction may be regarded as taking place in a voltaic cell, the two half cells being a $Cl_2,2Cl^-$ electrode and a Fe^{++}, Fe^{+++} electrode. The reaction is allowed to proceed to equilibrium, the total voltage or e.m.f. of the cell will then be zero, *i.e.*, the potentials of the two electrodes will be equal.

$$E^\circ_{Cl_2,2Cl^-} + \frac{0\cdot059}{2}\log\frac{[Cl_2]}{[Cl^-]^2} = E^\circ_{Fe^{++},\,Fe^{+++}} + \frac{0\cdot059}{1}\log\frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Now $E^\circ_{Cl_2,2Cl^-} = 1\cdot36$ volts and $E^\circ_{Fe^{++},\,Fe^{+++}} = 0\cdot75$ volts,

$$\text{hence } \log\frac{[Fe^{+++}]^2 \times [Cl^-]^2}{[Fe^{++}]^2 \times [Cl_2]} = \frac{0\cdot61}{0\cdot02965} = 20\cdot67 = \log K,$$

$$or \quad K = 4\cdot7 \times 10^{20}.$$

The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion, *i.e.*, a ferrous salt is almost completely oxidised by chlorine.

Consider now the more complex reaction :

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightleftharpoons Mn^{++} + 5Fe^{+++} + 4H_2O.$$

The equilibrium constant K is given by :

$$K = \frac{[Mn^{++}] \times [Fe^{+++}]^5}{[MnO_4^-] \times [Fe^{++}]^5 \times [H^+]^8},$$

The term $4H_2O$ is omitted since the reaction is carried out in dilute solution, and the water concentration may be assumed constant. The hydrogen ion concentration is taken as molar. The complete reaction may be divided into two half-cell reactions corresponding to the partial equations :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O \qquad \text{(i)},$$

$$\text{and} \qquad Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon \qquad \text{(ii)}.$$

For (i) as an oxidation-reduction electrode, we have :

$$E = E^\circ + \frac{0\cdot059}{5}\log\frac{[MnO_4^-] \times [H^+]^8}{[Mn^{++}]},$$

$$= 1\cdot48 + \frac{0\cdot059}{5}\log\frac{[MnO_4^-] \times [H^+]^8}{[Mn^{++}]}.$$

The partial equation (ii) may be multiplied by 5 in order to balance (i) electrically :

$$5Fe^{++} \rightleftharpoons 5Fe^{+++} + 5\epsilon \qquad \text{(ii}'\text{)}.$$

For (ii′) as an oxidation-reduction electrode :

$$E = E^\circ + \frac{0{\cdot}059}{5} \log \frac{[Fe^{+++}]^5}{[Fe^{++}]^5},$$

$$= 0{\cdot}75 + \frac{0{\cdot}059}{5} \log \frac{[Fe^{+++}]^5}{[Fe^{++}]^5}.$$

Combining the two electrodes into a cell, the e.m.f. will be zero when equilibrium is attained :

$$\textit{i.e.,}\ 1{\cdot}48 + \frac{0{\cdot}059}{5} \log \frac{[MnO_4^-] \times [H^+]^8}{[Mn^{++}]}$$

$$= 0{\cdot}75 + \frac{0{\cdot}059}{5} \log \frac{[Fe^{+++}]^5}{[Fe^{++}]^5},$$

$$\textit{or}\quad \log \frac{[Mn^{++}] \times [Fe^{+++}]^5}{[MnO_4^-] \times [Fe^{++}]^5 \times [H^+]^8} = \frac{5(1{\cdot}48 - 0{\cdot}75)}{0{\cdot}059} = 61{\cdot}9.$$

$$K = \frac{[Mn^{++}] \times [Fe^{+++}]^5}{[MnO_4^-] \times [Fe^{+++}]^5 \times [H^+]^8} = 1{\cdot}5 \times 10^{62}.$$

This result clearly indicates that the reaction proceeds virtually to completion. It is a simple matter to calculate the residual ferrous ion concentration in any particular case. Thus suppose we titrate 10 ml. $0{\cdot}1N$ potassium permanganate with approximately $0{\cdot}1N$ solution of ferrous ions in the presence of molar concentration of hydrogen ions. Let the volume of the solution at the equivalence point be 100 ml. Then $[Fe^{+++}] = 0{\cdot}01N$, since it is known that the reaction is practically complete, $[Mn^{++}] = 1/5 \times [Fe^{+++}] = 0{\cdot}002N$, and $[Fe^{++}] = x$. Let the excess of permanganate solution at the end point be one drop or 0·05 ml. ; its concentration will be $0{\cdot}05 \times 0{\cdot}1/100 = 5 \times 10^{-5}N = [MnO_4^-]$. Substituting these values in the equation :

$$K = \frac{(2 \times 10^{-3}) \times (1 \times 10^{-2})^5}{(5 \times 10^{-5}) \times x^5 \times 1^8} = 1{\cdot}5 \times 10^{62}.$$

$$\textit{or}\quad x = [Fe^{++}] = 5 \times 10^{-15}N.$$

For the general oxidation-reduction reaction :

$$a\,Ox_I + b\,Red_{II} \rightleftharpoons b\,Ox_{II} + a\,Red_I \qquad \text{(i)},$$

$$K = \frac{Red_I{}^a \times Ox_{II}{}^b}{Ox_I{}^a \times Red_{II}{}^b}.$$

It can readily be shown that the concentrations at the stoichiometric point when equivalent quantities of the two substances Ox_I and Red_{II} are allowed to react, are given by* :

$$\frac{Red_I}{Ox_I} = \frac{Ox_{II}}{Red_{II}} = \sqrt[a+b]{K} \qquad \text{(ii).}$$

This expression enables us to calculate the exact concentration at the equivalence point in any redox reaction of the type (i), and therefore the feasibility of a titration for quantitative analysis. Consider again the interaction between, say, $0{\cdot}1N$ solutions of potassium permanganate and a ferrous salt in the presence of molar sulphuric acid. The equilibrium constant of the reaction is $1{\cdot}5 \times 10^{62}$ (p. 107). At the equivalence point :

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \sqrt[5+1]{1{\cdot}5 \times 10^{62}} = \sqrt[6]{1{\cdot}5 \times 10^{62}} = 2{\cdot}3 \times 10^{10}\,.$$

Since the ferric ion concentration will then be *ca.* $0{\cdot}05N$, it is evident that for all practical purposes the reaction is a quantitative one.

It is clear from what has already been stated that standard oxidation potentials may be employed to determine whether redox reactions are sufficiently complete for their possible use in quantitative analysis. It must be emphasised, however, that these calculations provide no information as to the speed of the reaction, upon which the application of that reaction in practice will ultimately depend. This question must form the basis of a separate experimental study, which may include the investigation of the influence of temperature, variations of *p*H and of the concentrations of the reactants, and the influence of catalysts. Thus, theoretically, potassium permanganate should quantitatively oxidise oxalic acid in aqueous solution. It is found, however, that the reaction is extremely slow at the ordinary temperature, but is more rapid at about 80°C, and also increases in velocity when a little manganous ion has been formed, the latter apparently acting as a catalyst.

It is of interest to consider the calculation of the equilibrium constant of the general redox reaction (i), *viz.* :

$$a\,Ox_I + b\,Red_{II} \rightleftharpoons b\,Ox_{II} + a\,Red_I.$$

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* See for example, Kolthoff and Furman, *Potentiometric Titrations*, 1926, p. 65 (John Wiley).

The complete reaction may be regarded as composed of two oxidation-reduction electrodes, $a\mathrm{Ox_I}$, $a\mathrm{Red_I}$ and $b\mathrm{Ox_{II}}$, $b\mathrm{Red_{II}}$, combined together into a cell ; at equilibrium, the potentials of both electrodes are the same :

$$E_1 = \mathrm{E}_1^\circ + \frac{0{\cdot}0591}{n}\log\frac{[\mathrm{Ox_I}]^a}{[\mathrm{Red_I}]^a},$$

$$E_2 = E_2^\circ + \frac{0{\cdot}0591}{n}\log\frac{[\mathrm{Ox_I}]^b}{[\mathrm{Red_{II}}]^b}$$

At equilibrium, $E_1 = E_2$, hence :

$$E_1^\circ + \frac{0{\cdot}0591}{n}\log\frac{[\mathrm{Ox_I}]^a}{[\mathrm{Red_I}]^a} = E_2^\circ + \frac{0{\cdot}0591}{n}\log\frac{[\mathrm{Ox_{II}}]^b}{[\mathrm{Red_{II}}]^b};$$

$$\textit{or}\ \log\frac{[\mathrm{Ox_{II}}]^b \times [\mathrm{Red_I}]^a}{[\mathrm{Red_{II}}]^b \times [\mathrm{Ox_I}]^a} = \log K = \frac{n}{0{\cdot}0591}(E_1^\circ - E_2^\circ) \quad \text{(iii)}.$$

This equation may be employed to compute the equilibrium constant of any redox reaction, provided the two standard potentials E_1° and E_2° are known ; from the value of K thus obtained, the feasibility of the reaction in analysis may be ascertained.

I, 49. Change of the electrode potential during the titration of an oxidant and a reductant. Oxidation-reduction curve.— In Sections **I, 33** to **I, 36** we calculated the change in *p*H during the titration of an acid and a base, and we utilised the neutralisation curve thus obtained in order (*a*) to specify the most suitable indicator for use in the process, and (*b*) to compute the titration error in the quantitative neutralisation. We shall now attempt to carry out parallel calculations for oxidation-reduction processes. Let us study first a simple case which involves only the valency change of ions, and is theoretically independent of the hydrogen ion concentration. A suitable example, for purposes of illustration, is the titration of 100 ml. of $0{\cdot}1N$ ferrous iron with $0{\cdot}1N$ ceric cerium :

$$\mathrm{Ce^{++++}} + \mathrm{Fe^{++}} \rightleftharpoons \mathrm{Ce^{+++}} + \mathrm{Fe^{+++}}.$$

The quantity corresponding to *p*H is the ratio [Ox] / [Red]. We are concerned here with two systems, the ferrous-ferric ion electrode (i) and the cerous-ceric ion electrode (ii).

For (i) at 25°C.

$$E_1 = E_1^\circ + \frac{0{\cdot}0591}{1}\log\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]} = +\,0{\cdot}75 + 0{\cdot}0591\log\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}\,.$$

For (ii), at 25°C :

$$E_2 = E_2^\circ + \frac{0{\cdot}0591}{1}\log\frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}$$

$$= +\,1{\cdot}45 + 0{\cdot}0591 \log\frac{[\mathrm{Ce^{++++}}]}{[\mathrm{Ce^{+++}}]}\ .$$

The equilibrium constant of the reaction is given by (Section **I, 48**) :

$$\log K = \frac{[\mathrm{Ce^{+++}}] \times [\mathrm{Fe^{+++}}]}{[\mathrm{Ce^{++++}}] \times [\mathrm{Fe^{++}}]},$$

$$= \frac{1}{0{\cdot}0591}(1{\cdot}45 - 0{\cdot}75),$$

$$= 11{\cdot}84,$$

$$\textit{or} \qquad K = 7 \times 10^{11}.$$

The reaction is therefore virtually complete.

During the addition of the ceric solution up to the equivalence point, its only effect will be to oxidise the ferrous iron (since K is large) and consequently change the ratio $[\mathrm{Fe^{+++}}]/[\mathrm{Fe^{++}}]$. When 10 ml. of the oxidising agent have been added, $[\mathrm{Fe^{+++}}] / [\mathrm{Fe^{++}}] = 10/90$ (approx.),

and $E_1 = 0{\cdot}75 + 0{\cdot}0591 \log 10/90 = 0{\cdot}75 + 0{\cdot}056 = 0{\cdot}69$ volt.

With 50 ml. of the oxidising agent, $E_1 = E_1^\circ = 0{\cdot}75$ volt.

With 90 ml., $E_1 = 0{\cdot}75 + 0{\cdot}0591 \log 90/10 = 0{\cdot}81$ volt.

With 99 ml., $E_1 = 0{\cdot}75 = 0{\cdot}0591 \log 99/1 = 0{\cdot}87$ volt.

With 99·9 ml., $E_1 = 0{\cdot}75 + 0{\cdot}0591 \log 99{\cdot}9/0{\cdot}1 = 0{\cdot}93$ volt.

At the equivalence point (100·0 ml.) $[\mathrm{Fe^{+++}}] = [\mathrm{Ce^{+++}}]$ and $[\mathrm{Ce^{++++}}] = [\mathrm{Fe^{++}}]$, and the electrode potential is given by* :

$$\frac{E_1^\circ + E_2^\circ}{2} = \frac{0{\cdot}75 + 1{\cdot}45}{2} = 1{\cdot}10 \text{ volts.}$$

---

* For a deduction of this expression and a discussion of the approximations involved, see Kolthoff and Furman, *Potentiometric Titrations*, 1926, p. 109. It can similarly be shown (*loc. cit.* p. 107) that for the reaction :

$$a\,\mathrm{Ox_I} + b\,\mathrm{Red_{II}} \rightleftharpoons b\,\mathrm{Ox_{II}} + a\,\mathrm{Red_I},$$

the potential at the equivalence point is given by :

$$E_e = \frac{bE_1^\circ + aE_2^\circ}{a + b},$$

where E_1° refers to $\mathrm{Ox_I}$, $\mathrm{Red_I}$, and E_2° to $\mathrm{Ox_{II}}$, $\mathrm{Red_{II}}$.

The subsequent addition of the ceric solution will merely increase the ratio $[Ce^{++++}]/[Ce^{+++}]$. Thus :

with 100·1 ml., $E_1 = 1{\cdot}45 + 0{\cdot}0591 \log 0{\cdot}1/100 = 1{\cdot}27$ volts ;
with 101 ml., $E_1 = 1{\cdot}45 + 0{\cdot}0591 \log 1/100 = 1{\cdot}33$ volts ;
with 110 ml., $E_1 = 1{\cdot}45 + 0{\cdot}0591 \log 10/100 = 1{\cdot}39$ volts ;
with 190 ml., $E_1 = 1{\cdot}45 + 0{\cdot}0591 \log 90/100 = 1{\cdot}45$ volts.

These results are plotted graphically in Fig. 1-16.

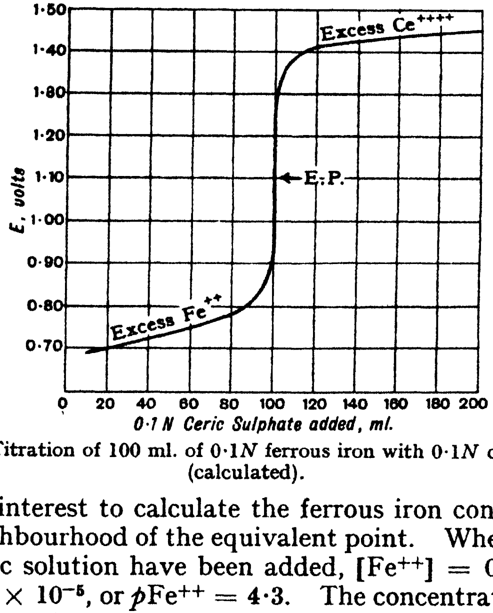


FIG. 1-16. Titration of 100 ml. of 0·1*N* ferrous iron with 0·1*N* ceric sulphate (calculated).

It is of interest to calculate the ferrous iron concentration in the neighbourhood of the equivalent point. When 99·9 ml. of the ceric solution have been added, $[Fe^{++}] = 0{\cdot}1 \times 0{\cdot}1/199{\cdot}9 = 5 \times 10^{-5}$, or $pFe^{++} = 4{\cdot}3$. The concentration at the equivalence point is given by (Section **I, 48**) :

$$[Fe^{+++}]/[Fe^{++}] = \sqrt{K} = \sqrt{7 \times 10^{11}} = 8{\cdot}5 \times 10^{5}.$$

Now $[Fe^{+++}] = 0{\cdot}05N$, hence $[Fe^{++}] = 5 \times 10^{-2}/8{\cdot}5 \times 10^{5} = 6 \times 10^{-8}N$, or $pFe^{++} = 7{\cdot}2$. Upon the addition of 100·1 ml. of ceric solution, the oxidation potential (*vide supra*) is 1·27 volts. The $[Fe^{+++}]$ is practically unchanged at $5 \times 10^{-2}N$, and we may calculate $[Fe^{++}]$ with sufficient accuracy for our purpose from the equations :

$$E = E^{\circ}_{1} + 0{\cdot}0591 \log \frac{[Fe^{+++}]}{[Fe^{++}]},$$

$$1{\cdot}27 = 0{\cdot}75 + 0{\cdot}0591 \log \frac{5 \times 10^{-2}}{[Fe^{++}]}.$$

$$[Fe^{++}] = 1 = 10^{-10}, \quad \text{or } pFe^{++} = 10.$$

Thus $p\mathrm{Fe}^{++}$ changes from 4·3 to 10 between 0·1 per cent before to 0·1 per cent after the stoichiometric point. These quantities are of importance in connexion with the use of indicators for the detection of the equivalence point.

It is evident that the abrupt change of the potential in the neighbourhood of the equivalence point is dependent upon the standard potentials of the two oxidation-reduction systems that are involved, and therefore upon the equilibrium constant of the reaction; it is independent of the concentrations unless these are extremely small. The change in oxidation potential for a number of typical oxidation-reduction systems is exhibited graphically in Fig. 1-17. For the MnO_4^-, Mn^{++} system and others which are dependent upon the *p*H of the solution, the hydrogen ion concentration is assumed to be molar: lower acidities give lower potentials. The value at 50 per cent oxidised form will of course correspond to the standard oxidation potential. As an indication of the application of the curves, we may take the titration of ferrous iron with potassium dichromate. The titration curve would follow that of the ferrous-ferric system until the end point was reached, then it would rise steeply and continue along the curve for the dichromate-chromic system: the potential at the equivalence point can be computed as already described (p. 110).

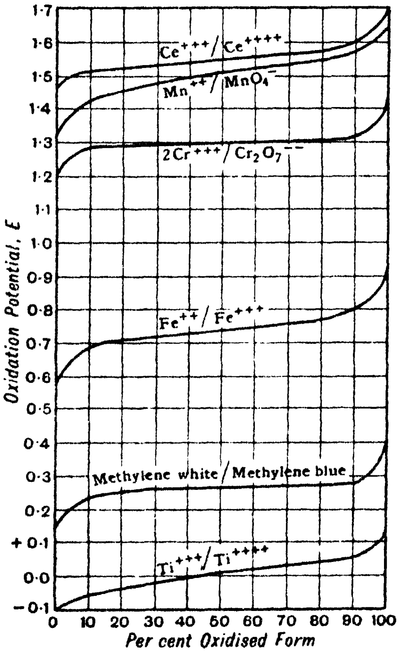


FIG. 1-17.

I, 50. Indicators for the detection of the end point in oxidation-reduction titrations.—A. Internal oxidation-reduction indicators. We have already seen (Sections **I, 32–34**) that acid-base indicators are employed to mark the sudden change in *p*H during acid-base titrations. Similarly an oxidation-reduction indicator should mark the sudden change in the oxidation potential in the neighbourhood of the equivalence point in an oxidation-reduction titration. The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant, and which exhibits a sharp, readily detectable colour change. The subject is still in its infancy, and thus far only a few such indicators have been discovered.

An oxidation-reduction indicator is a compound which has different colours in the oxidised and reduced forms :

$$\mathrm{In_{Ox}} + n\epsilon \rightleftharpoons \mathrm{In_{Red}}.$$

The oxidation and reduction of the indicator should be reversible. Many organic dyestuffs belong to this class ; the leuco compounds obtained on reduction are usually colourless, and are converted by oxidation into the coloured dyes. If such an indicator is added to any redox system, for example, one containing ferric and ferrous ions, the following equilibrium will be present :

$$\mathrm{Fe^{+++}} + \mathrm{In_{Red}} \rightleftharpoons \mathrm{Fe^{++}} + \mathrm{In_{Ox}}.$$

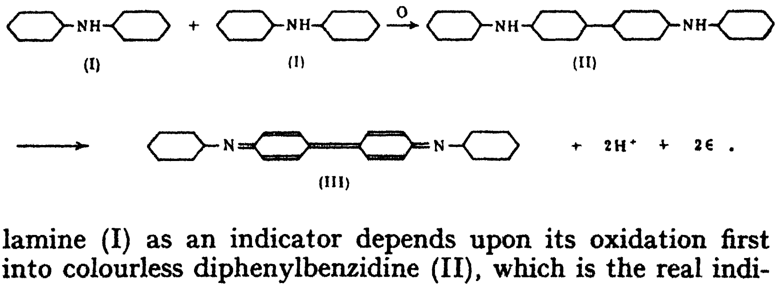
If the quantity of indicator added is small, it will have little effect on the main ferric-ferrous system, and it will adjust itself so that its potential is the same as that of the solution in which it is placed. The colour of the indicator system will depend upon this potential. When the concentrations of $\mathrm{In_{Ox}}$ and $\mathrm{In_{Red}}$ are equal, the colour will be intermediate between those of the two extreme states, and the potential is equal to the standard potential of the indicator E°_{In}. It can be shown that if the potential is about 0·05 volt greater than E°_{In}, the indicator will be about 90 per cent oxidised and its colour will be indistinguishable to the eye from that of the oxidised form (compare Section **I, 27**) ; if the potential is $(E^\circ_{\mathrm{In}} - 0{\cdot}05)$ volt, then about 90 per cent of the indicator will be in the reduced form and it will exhibit its almost completely reduced colour. Thus the colour change for a redox indicator will be over the potential range $(E^\circ_{\mathrm{In}} - 0{\cdot}05)$ to $(E^\circ_{\mathrm{In}} - 0{\cdot}05)$ volts. For a sharp colour change at the end point, E°_{In} should differ by at least 0·15 volt from the other systems involved in the reaction.

One of the best oxidation-reduction indicators is the ortho-phenanthroline ferrous ion. The base ortho-phenanthroline combines readily in solution with ferrous salts in the molecular ratio 3 base : 1 ferrous ion forming the intensely red tri-ortho-phenanthroline ferrous ion; with strong oxidising agents the ferric complex ion is formed, which has a pale blue colour. The colour change is a very striking one.

$$\underset{\textit{deep red}}{[Fe(C_{12}H_8N_2)_3]^{++}} \rightleftharpoons \underset{\textit{pale blue}}{[Fe(C_{12}H_8N_2)_3]^{+++}} + \epsilon.$$

The oxidation potential is 1·14 volts. The indicator is of great value in the titration *inter alia* of ferrous salts and other substances with ceric sulphate solutions. It is prepared by dissolving ortho-phenanthroline hydrate (molecular weight = 198·1) in the calculated quantity of 0·02*M* acid-free ferrous sulphate, and is therefore tri-ortho-phenanthroline ferrous sulphate. One drop is usually sufficient in a titration: this is equivalent to less than 0·01 ml. of 0·1*N* oxidising agent, and hence the indicator blank is negligible. The only disadvantage of this indicator is that it is somewhat expensive. It may be replaced in many titrations by the less costly *N*-phenylanthranilic acid (see Section **III, 73**), which has an oxidation potential of 1·08 volts. Xylene cyanol FF ($E^\circ_{In} > 1{\cdot}0$ volt) may also be employed.

Mention should be made of one of the earliest internal indicators. This is a one per cent solution of diphenylamine in concentrated sulphuric acid, and was introduced by Knop (1924) for the titration of ferrous salts with potassium dichromate solution. To obtain a satisfactory end point (an intense blue-violet colouration), phosphoric acid must be present; this forms a complex with the ferric ions, thereby reducing the concentration of the latter, and consequently the actual potential of the ferric-ferrous system is reduced well below the normal value of 0·75 volt. The action of diphenylamine (I) as an indicator depends upon its oxidation first into colourless diphenylbenzidine (II), which is the real indicator and is reversibly further oxidised to diphenylbenzidine-violet (III). Under certain conditions there is formed as an intermediate product a very slightly soluble green compound



which is usually considered to be a molecular compound of diphenylbenzidine and diphenylbenzidine-violet.

A solution of diphenylbenzidine in concentrated sulphuric acid acts similarly to diphenylamine. The oxidation potential of the system II, III is 0·76 volt. It is therefore evident that a lowering of the potential of the ferrous-ferric system is necessary, as already mentioned, in order to obtain a sharp colour change. The disadvantage of diphenylamine and of diphenylbenzidine is their slight solubility in water. This has been overcome by the use of the soluble barium or sodium diphenylamine sulphonate, which are employed in 0·2 per cent solution. The oxidation potential ($E°_{\text{In}}$) is slightly higher (0·83 volt), and the oxidised form has a reddish-violet colour resembling that of potassium permanganate, but the colour slowly disappears on standing ; phosphoric acid must still be present in order to lower the oxidation potential of the system. The addition of phosphoric acid may be avoided by the use of ortho-phenanthroline ferrous ion, *N*-phenylanthranilic acid or xylene cyanol FF as indicators.

At this stage reference may be made to **potential mediators,** *i.e.*, substances which undergo reversible oxidation-reduction and reach equilibrium *rapidly*. If we have a mixture of two ions, say M^{++} and M^{+}, which reaches equilibrium slowly with an inert electrode, and a very small quantity of a ceric salt is added, then the reaction :

$$M^{+} + Ce^{++++} \rightarrow M^{++} + Ce^{+++}$$

takes place until the tendency of M^{+} to be oxidised to M^{++} is exactly balanced by the tendency of Ce^{+++} to be oxidised to Ce^{++++}, that is, until the M^{++}, M^{+} and Ce^{++++}, Ce^{+++} potentials are equal. A platinum or other inert electrode rapidly attains equilibrium with the cerous and ceric ions and will soon register a stable potential which is also that due to the $M^{++} + \epsilon \rightleftharpoons M^{+}$ system. If the potential mediator is employed in small amount, then a negligible quantity of M^{+} is converted into M^{++} when equilibrium is reached and the measured potential may be regarded as that of the original system. Potential mediators are of course useful in the measurement of the oxidation-reduction potentials of redox systems ; in this connexion mention may be made of the use of potassium iodide ($\equiv$ iodide-iodine system) in the arsenate-arsenite system in acid solution and of ceric carbonate ($\equiv$ ceric-cerous system) in the arsenate-arsenite system in alkaline solution. It is evident that redox indicators (*e.g.*, ortho-phenanthroline ferrous ion) may act as potential mediators.

B. The reagent may serve as its own indicator. This is well illustrated by potassium permanganate. One drop (0·05 ml.) of excess of, say, 0·1*N* potassium permanganate will impart a visible pink colouration to several hundred ml. of solution, even in the presence of slightly coloured ions, such as ferric ions. The colour of ceric sulphate and of iodine solutions have also been employed in the detection of end points, but the colour change is not so marked as for potassium permanganate; here, however, sensitive internal indicators (ortho-phenanthroline ferrous ion or *N*-phenylanthranilic acid and starch respectively) are available.

This method has the drawback that an excess of oxidising agent is always present at the end point. For work of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerably reduced by performing the standardisation and determination under similar experimental conditions.

C. External indicators. The best known example of an external indicator in a redox process is the spot test method for the titration of ferrous iron with standard potassium dichromate solution. Near the equivalence point, drops of the solution are removed and brought into contact with dilute, freshly prepared potassium ferricyanide solution on a spot plate. The end point is reached when the first drop fails to give a blue colouration. Another example is provided by the titration of zinc ions with standard potassium ferrocyanide solution; here a solution of uranyl acetate or nitrate is the external indicator, and titration is continued until a drop of the solution just imparts a brown colour to the indicator. External indicators are gradually being superseded by the more satisfactory internal oxidation-reduction indicators: thus in the first example ortho-phenanthroline ferrous ion or *N*-phenylanthranilic acid is suitable, whilst for the second diphenylamine or diphenylbenzidine may be used.

D. Potentiometric methods. These are discussed in the following Section. They can usually be applied where no satisfactory indicator is available.

I, 51. Potentiometric titration.—The various visual methods, dependent largely upon the use of indicators, for the detection of the end point in titrations have already been discussed. We shall now deal with a physico-chemical method which may be applied not only to those cases where suitable indicators are available, but also to those in which the visual indicator method fails or is of limited accuracy, *e.g.*, for coloured or for very dilute solutions ; the procedure is termed **potentiometric titration.** This method may often be employed for the determination of two or more constituents in a single operation. Thus a mixture of iodide and chloride may be titrated with silver nitrate solution ; the first point of inflexion is the equivalence point of the iodide reaction and the second inflexion point is that for the chloride reaction (compare Fig. 1-12).

The theory of potentiometric titration is very similar to that already given for ordinary titrations. It has been shown (Section **I, 43**) that the potential of a metal electrode and a solution of its own ions at 25°C is given by the expression :

$$E_{25^\circ} = E^\circ + \frac{0{\cdot}0591}{n}\log c_{i+} \qquad \text{(i)},$$

where E° is the standard potential of the metal, n the valency of the ions, and c_{i+} is the ionic concentration (strictly, this should be the ionic activity). If we write c_{i+} in the exponential form, *i.e.*,

$$-\log[\mathrm{Me}^{n+}] = p\mathrm{Me}^{n+}, \text{ the equation becomes:}$$

$$E_{25^\circ} = E^\circ - \frac{0{\cdot}0591}{n}\,p\mathrm{Me}^{n+} \qquad \text{(i}'\text{)}.$$

The expression for a hydrogen electrode at 25°C is :

$$E_{25^\circ} = E^\circ_{\mathrm{H}} - 0{\cdot}0591\,p\mathrm{H} \qquad \text{(ii)},$$

where E°_{H} is the standard potential of the normal hydrogen electrode. For an oxidation-reduction electrode, the expression is :

$$E_{25^\circ} = E^\circ + \frac{0{\cdot}0591}{n}\log\frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \qquad \text{(iii)},$$

where E° is the standard oxidising potential, n the number of electrons gained by the oxidant in being converted into the reductant, and [Ox] and [Red] are the concentrations (strictly, the activities) of the oxidant and reductant respectively.

The determination of E is the essence of potentiometric titration : this may be used either to measure the ionic (or [Ox] / [Red]) concentration of a solution, or, what is more important for our present purpose, to follow the changes in ionic concentration or of the ratio [Ox] / [Red] during the course of a titration.

Since E°_H, the normal potential for hydrogen, *viz.*, the potential of the hydrogen electrode immersed in a solution of hydrogen ions of unit activity at one atmosphere pressure, is taken arbitrarily as zero at all temperatures, expression (ii) reduces to :

$$E = -0{\cdot}0591\ p\mathrm{H} \quad (\text{at } 25^\circ\mathrm{C}^*)$$

on this scale. On theoretical grounds, therefore, the determination of the hydrogen ion concentration is the simplest case to deal with, and it is proposed to discuss this first.

I, 52. Determination of *p*H.—A. The hydrogen electrode. A typical hydrogen electrode has already been described (Section **I, 43**). For routine work, the most convenient source of hydrogen is the compressed gas, sold in cylinders ; by means of a suitable reducing valve, a steady stream of hydrogen gas can be readily obtained. The gas should be passed through all-glass wash bottles containing respectively alkaline potassium permanganate solution, alkaline pyrogallol solution and purified glass wool before reaching the electrode. If a hydrogen electrode is immersed in a solution the *p*H of which is to be determined, and the half cell coupled with a molar hydrogen electrode by means of a potassium chloride bridge (Fig. 1-18) in order to eliminate the liquid junction potential,[†] the e.m.f. of the resultant cell :

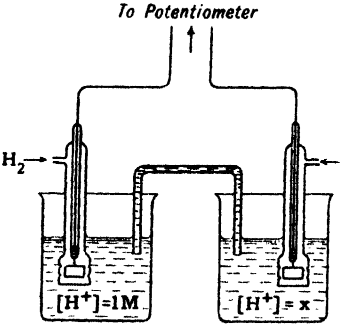


FIG. 1-18.

$$\mathrm{Pt} \mid \underset{a\,=\,1}{\mathrm{H_2,\ H^+}} \parallel \underset{a\,=\,x}{\mathrm{H_2,\ H^+}} \mid \mathrm{Pt},$$

---

* At any other temperature T, this becomes :

$$E = -0{\cdot}0001982T.\ p\mathrm{H},$$

where T is the absolute temperature.

[†] The open ends of the bridge are plugged tightly with pure filter paper in order to minimise diffusion effects. Alternatively, a jelly of 3 per cent agar in saturated potassium chloride solution may be used.

may be measured by means of a potentiometer (see below). The e.m.f. of this concentration cell (see Section **I, 44**) at 25°C is given by :

$$E = \frac{0{\cdot}0591}{n} \log \frac{c_2}{c_1},$$

$$= \frac{0{\cdot}0591}{1} \log \frac{1}{[\mathrm{H}^+]},$$

$$= 0{\cdot}0591\ p\mathrm{H};$$

$$\text{or}\quad p\mathrm{H} = E/0{\cdot}0591.$$

The use of the molar hydrogen electrode as a standard electrode or half cell presents certain practical difficulties. It is usual to employ some form of the calomel electrode as a secondary standard half-cell. A **calomel electrode** is one in which mercury and calomel are covered with potassium chloride of definite concentration ; this may be $0{\cdot}1N$, N, $3{\cdot}5N$ or saturated. The potassium chloride solution must be saturated with calomel. The potential of, say, the saturated calomel electrode (*i.e.*, that prepared with saturated potassium chloride solution) must first be determined with reference to the molar hydrogen electrode. Let this value be designated $E_{cal.\ sat.}$. For the measurement of hydrogen ion concentration, we then employ the cell :

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl\ (satd.)} \parallel \mathrm{H^+},\ \mathrm{H_2} \mid \mathrm{Pt}.$$

Let the resultant e.m.f. be $E_{obs.}$. Then, at 25°C :

$$E_{obs.} = E_{cal.\ sat.} - 0{\cdot}0591 \log [\mathrm{H}^+] ;$$

$$p\mathrm{H} = \frac{E_{obs.} - E_{cal.\ sat.}}{0{\cdot}0591}.$$

The value of $E_{cal.\ sat.}$ is 0·246 volt at 25°C.

Various forms of the calomel electrode are illustrated in Fig: I-19. One of these, (*a*), will be described in detail ; the others will then be self-evident. It consists of a glass vessel provided with a bent side tube **A** and another side tube **B**, over the end of which a piece of rubber tubing is placed which can be closed by a spring or screw clip. Electrical connection with the electrode is made by means of a platinum wire, sealed through a glass tube **C** ; the latter contains a little pure mercury into which an amalgamated copper wire dips. To set up the electrode, a saturated solution of analytically pure potassium chloride containing some of the solid salt is

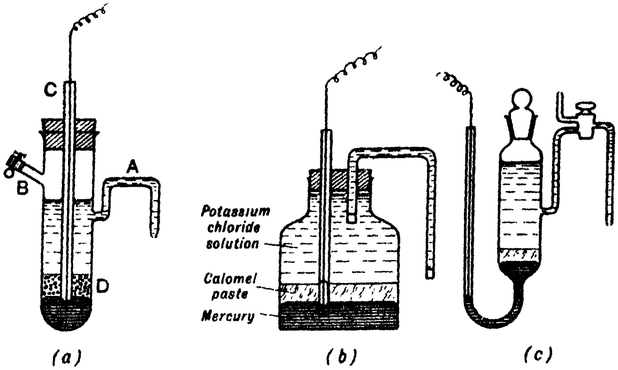


FIG. 1-19.

first prepared. Pure mercury to a depth of 0·5 to 1 cm. is placed in the bottom of the dry electrode vessel ; the mercury is then covered with a layer of calomel paste **D.** The latter is prepared by rubbing pure calomel, mercury and saturated potassium chloride solution together in a glass mortar ; the supernatant liquid is poured off and the rubbing process repeated twice with fresh quantities of saturated potassium chloride solution. The rubber bung carrying the glass tube and platinum wire is then inserted, care being taken that the platinum wire dips into the mercury. The vessel is then filled with a saturated solution of potassium chloride (previously saturated with calomel by shaking with the solid salt) by drawing in the solution through the bent tube **A,** and then closing the rubber tube **B** with a clip. The electrode is then ready for use. In electrode (*b*), the siphon tube or salt bridge may be filled with a jelly of 3 per cent agar in saturated potassium chloride solution. The electrode (*c*) is suitable for precision work ; it has a 3-way stop-cock for flushing away the contaminated potassium chloride after it has been employed in a titration.

The most satisfactory method for the measurement of the e.m.f. of a cell is that known as **Poggendorff's compensation method,** an outline of which is given below. The principle of the method is to balance the unknown e.m.f. against a known e.m.f., which can easily be varied. When these two e.m.f.s are exactly equal, no current will flow through a galvanometer placed in the circuit : the galvanometer is therefore employed as a null instrument. The essential details are shown in Fig. 1-20.

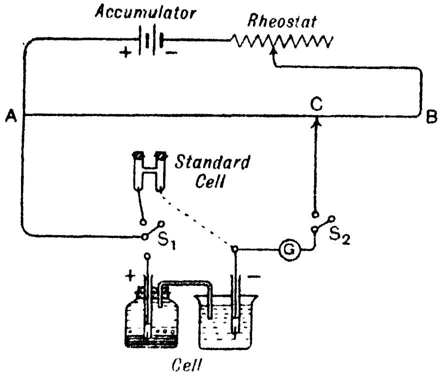


FIG. 1-20.

A 2- or 4-volt accumulator furnishes the opposing e.m.f.; this is connected in series with a rheostat and with the terminals of a slide wire **AB**. The latter is a thin wire of uniform cross section and is often termed the "potentiometer wire." The cell, the e.m.f. of which is to be determined, is connected to one end **A** of the slide wire, and through a galvanometer **G** and a key $\mathbf{S_2}$ to a sliding contact **C,** which can be moved along **AB.** A special double-throw switch $\mathbf{S_1}$ may be provided to permit the standard cell to be placed in the circuit. In connecting the accumulator and the cell to the bridge, it is essential that the positive poles should be connected to the same end of the bridge wire; the unknown cell will then send a current through the circuit in a direction opposite to that furnished by the accumulator.

If we assume that the potentiometer wire has uniform cross section and resistance, then the fall of potential along the slide wire will be uniform. The difference of potential between **A** and any point **C** will be proportional to the length **AC,** and will be equal to the fraction **AC/AB** of the total fall of potential along the wire. If the unknown cell is now placed in circuit and the position of **C** so adjusted that when the switch $\mathbf{S_2}$ is depressed, no current passes through the galvanometer **G,** then the e.m.f. of the cell is equal to that of the accumulator multiplied by **AC/AB.** For most potentiometric work, only *changes* of potential are required, so that variations of the length **AC** are all that are required during a titration.

In general, however, the e.m.f. of the accumulator is not quite constant. A standard cell is employed. This is usually a Weston cell which has an e.m.f. of 1·0183 volts at 20° C or

$$1{\cdot}0183 - 0{\cdot}0000406\,(t - 20°)$$

at any other temperature t°C. If the standard cell is placed in circuit by means of the switch $\mathbf{S_1}$ and the point of balance

C′ on the bridge is determined, then the unknown e.m.f. may be calculated from the relation :

$$\frac{\mathbf{AC}}{\mathbf{AC'}} = \frac{\text{e.m.f. of unknown cell}}{\text{e.m.f. of standard cell}}.$$

For approximate work, the slide wire **AB** may consist of an ordinary meter bridge, and the indicating instrument may be a milli-ammeter. It is preferable, however, to employ a commercial type of potentiometer, which utilise the more compact spiral type of bridge wire.* The most convenient type of indicating instrument is the direct vision type of mirror galvanometer ; the galvanometer and lamp scale are incorporated in a blackened wooden box and the " spot " is clearly visible in daylight.† The rheostat in the commercial potentiometer provides for the drop of potential along the slide wire. If the bridge is divided into, say, 2000 equal parts, then the rheostat may be adjusted with the standard cell in circuit and with the sliding contact **C** at a position corresponding to 1018·3 divisions so that no current flows through the galvanometer. The position of the sliding contact will then give the e.m.f. of any unknown cell directly in millivolts. It is usual for the rheostat to contain both coarse and fine adjustments : the fine adjustment may be used to compensate for the slight variations of the accumulator during the measurements.

The **hydrogen electrode** cannot be used in solutions containing oxidising agents, *e.g.*, permanganate, nitrate, ceric and ferric ions, or of other substances capable of reduction such as unsaturated organic compounds, or in the presence of sulphides, compounds of arsenic etc. (catalytic poisons) which destroy the catalytic property of platinum black. It is also unsatisfactory in the presence of salts of the noble metals, *e.g.*, copper, silver and gold, and also in solutions containing lead, cadmium and thallous salts. There are many other electrodes which are more convenient to use in the range in which they are applicable. Some of these will be described below.

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* Excellent potentiometers are made by H. Tinsley and Co. of London, The Cambridge Instrument Co. of London, and the Leeds and Northrup Co. of Philadelphia, U.S.A. Upon request, these firms will supply pamphlets containing full details, including the wiring circuit, of their instruments.

† The author has found that marketed by H. Tinsley and Co. of London very convenient in practice ; many other similar types are available commercially.

B. The quinhydrone electrode. The preparation of reproducible hydrogen electrodes is a comparatively tedious process and, moreover, the electrode has certain limitations (see previous paragraph). E. Biilmann (1921) has introduced the **quinhydrone electrode**: this renders the determination of *p*H a rapid and simple process, and does not require the use of hydrogen gas. Quinhydrone is a compound of quinone and hydroquinone, and in solution is decomposed into equimolecular quantities of these substances:

$$\underset{\text{quinhydrone}}{C_6H_4O_2.C_6H_4(OH)_2} = \underset{\text{quinone}}{C_6H_4O_2} + \underset{\text{hydroquinone}}{C_6H_4(OH)_2}.$$

Quinone and hydroquinone form a reversible oxidation-reduction system which may be represented as:

$$C_6H_4O_2 + 2H^+ + 2\epsilon \rightleftharpoons C_6H_4(OH)_2.$$

If an inert electrode, such as platinum, is immersed in the system, the potential is given by (Section **I, 47**):

$$\begin{aligned} E &= E_o + \frac{RT}{2F} \log_e \frac{a_Q \,.\, a_{H^+}{}^2}{a_{H_2Q}}, \\ &= E_o + \frac{RT}{2F} \log_e \frac{a_{H_2Q}}{a_Q} + \frac{RT}{F} \log_e a_{H^+}, \end{aligned}$$

where a_Q, a_{H^+} and a_{H_2Q} are the activities of the quinone, hydrogen ions and hydroquinone respectively, and E_o is the standard potential referred to the molar hydrogen electrode. Now under those conditions in which quinhydrone dissociates to give equimolecular quantities of quinone and hydroquinone, the ratio of the activities may be regarded as constant, hence:

$$E = E_o + \frac{RT}{F} \log_e a_{H^+} \qquad \text{(i)}.$$

E_o has been determined in the usual manner by direct reference to the molar hydrogen electrode, and has a value of 0·7044 volt at 18°C and 0·6991 volt at 25°C. By making the usual substitution for the known values of the constants in equation (i), we have, at 25°C:

$$E = 0{\cdot}6991 + 0{\cdot}0591 \log a_{H^+} \qquad \text{(i')}.$$

Thus the potential of the quinhydrone electrode changes with the hydrogen ion activity in a manner which is exactly similar to that of the hydrogen electrode.

For convenience, a calomel electrode often replaces the molar hydrogen electrode as the other half cell. The complete cell is then:

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2, \text{KCl (satd.)} \parallel \text{Solution, quinhydrone} \mid \text{Pt}.$$

The potential of the saturated calomel electrode, $E_{cal.\,sat.}$, against the molar hydrogen electrode is 0·2458 volt at 25° C.

$$\begin{aligned} \text{Hence } E_{obs.} &= E_{quinhydrone} - E_{cal.\ sat.}, \\ &= 0{\cdot}6991 + 0{\cdot}0591 \log\,[\mathrm{H}^+] + 0{\cdot}2458, \\ &= 0{\cdot}4533 + 0{\cdot}0591 \log\,[\mathrm{H}^+]. \end{aligned}$$

$$p\mathrm{H} = -\log\,[\mathrm{H}^+] = \frac{0{\cdot}4533 - E_{obs.}}{0{\cdot}0591} \qquad \text{(ii)}.$$

To carry out a determination of the hydrogen ion concentration of a solution, about one gram of quinhydrone[*] per 100 ml. of solution is added, and the solution stirred. A bright platinum electrode is immersed in the solution and the quinhydrone electrode combined in a cell with a saturated calomel electrode ; a saturated solution of potassium chloride or, less accurately but perhaps more conveniently, a jelly of 3 per cent agar in saturated potassium chloride solution may be used as the salt bridge. The *p*H is then calculated by equation (ii). It may be mentioned that the platinum electrode should be highly polished and clean ; it is best cleaned by treatment with hot chromic acid mixture, then thoroughly washed with distilled water, and ignited in an *alcohol* flame.

An alternative method is to use a solution of known *p*H as standard and to combine the two quinhydrone electrodes into a concentration cell :

Pt | Solution of unknown *p*H, quinhydrone || Solution of known *p*H, quinhydrone | Pt.

$$\text{Then} \quad E_{obs.} = \frac{0{\cdot}0591}{1} \log \frac{c_2}{c_1} \text{ at } 25^\circ \text{ C},$$

where c_2 and c_1 are the respective hydrogen ion concentrations ;

$$p\mathrm{H}_2 = \frac{p\mathrm{H}_1 - E_{obs.}}{0{\cdot}0591},$$

where $p\mathrm{H}_2$ refers to c_2 and $p\mathrm{H}_1$ to c_1. If $p\mathrm{H}_2$ is known, $p\mathrm{H}_1$ can be readily calculated.

The advantages of the quinhydrone electrode are : (i) it attains equilibrium rapidly ; (ii) it may be used in many solutions in which the hydrogen electrode is inapplicable, *e.g.*, in solutions of zinc, cadmium, tin, lead, copper and nickel salts, dilute nitric acid, and in solutions of unsaturated organic acids, of amino acids and of alkaloids ; (iii) it is not so readily incapacitated as the hydrogen electrode. Its disadvantages are : (i) it cannot be used in solutions of *p*H greater than about *p*H 8 (this is because hydroquinone behaves as a weak dibasic acid and then begins to have an effect on the *p*H of the solution ; moreover, this will also affect the molecular ratio of quinone to hydroquinone since the concentration of the undissociated hydroquinone becomes reduced) ; (ii) the potential may be slightly affected by large concentrations of neutral salts—the " salt error " : this error, however, is negligible under the conditions that the electrode is normally used.

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[*] Pure quinhydrone (analytical reagent quality) is available commercially. It can also be readily prepared by oxidation of hydroquinone with ferric ammonium sulphate at 65° C.

C. The glass electrode. F. Haber and Z. Klemensiewicz (1909) found that the potential difference between a thin glass surface and the solution in which it was immersed varied in a regular manner with the *p*H of the solution. This remarkable fact has been utilised in recent years as the basis of a valuable method for measuring the *p*H of solutions. Ordinary soft glass has too great a resistance to be of any great value. A suitable glass has the composition 6 per cent CaO, 22 per cent Na_2O and 72 per cent SiO_2 ; this is the lowest melting point glass which can be prepared using these three ingredients. The glass made by the Corning Company of America, known as Corning No. 015 glass, is also suitable. Two types of electrode are employed. In the first type (*a* in Fig. 1-21), a tube **A** of the special glass is blown out at the lower end into an extremely thin bulb **B**. In the second type (*b* in Fig. 1-21), due to MacInnes and Dole, a very thin membrane of the special glass is sealed on to the end of a glass tube, which is smooth and square. This is accomplished by first blowing a large thin bubble on the end of the special glass tubing ; the end of **A** is heated to redness and then pressed against the thin bulb. The heat in the tube **A** is sufficient to fuse the thin membrane into place. Considerable experience is required to prepare satisfactory electrodes of type (*b*) ; in general, particularly for routine work, the bulb type is to be preferred. These are readily prepared and can also be purchased. The glass electrode is filled to a depth of 1

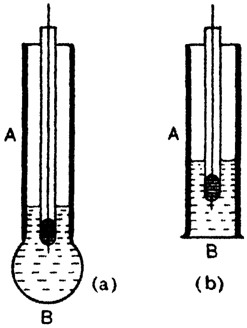

Fig. 1-21.

to 2 cms. with 0.1*N* hydrochloric acid and a little quinhydrone or with a buffer mixture (such as sodium acetate—acetic acid mixture), and a clean platinum wire sealed through a glass tube is inserted to make electrical connexion. The bulb is then immersed in a solution of which the *p*H is to be measured; a calomel (or other convenient electrode) completes the cell. Owing to the high resistance (5–50 megohms) of the glass electrode, special methods must be adopted for measuring the e.m.f. of the cell. Perhaps the most convenient in practice is to employ an ordinary commercial potentiometer coupled with an appropriate amplifying unit* and a suitable ballistic galvanometer.* Special precautions must be taken to avoid electrical leakage, for example, the upper part of the tube **A** should be waxed and, if possible, the cell should be immersed in a thermostat containing a special paraffin oil. When not in use, the electrodes must be kept immersed in water.

If the glass electrode described above is used, the potential of the electrode at 25°C is given by:

$$E = K - 0{\cdot}0591\,p\text{H},$$

where K is a constant; this expression holds up to a *p*H of about 10. The value of K is most simply determined by immersing the glass electrode in buffer solutions, coupling with a calomel or hydrogen electrode and measuring the e.m.f.; this standardisation must be carried out at least once a day since K varies slightly. Variation from this expression occurs at higher *p*H values, but by calibration with suitable buffer solutions, the glass electrode may be employed up to a *p*H of 12.

The advantages of the glass electrode are: (i) no chemical is added to the solution; (ii) the e.m.f. is independent of oxidation-reduction potentials; (iii) it is not affected by the colour or turbidity of solutions; (iv) it can be used in unbuffered solutions; (v) its most useful range is *p*H 0 to 10, which may be extended by careful calibration to *p*H 12; (vi) it attains equilibrium comparatively rapidly. Its disadvantages are : (i) the high electrical resistance of the glass which necessitates special measuring equipment and also special precautions to prevent electrical leakage ; (ii) its fragility (see, however, footnote above and also Plate I).

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* Such an amplifying unit is obtainable from H. Tinsley and Co., of Werndee Hall, London, England, as is also the ballistic galvanometer. A comprehensive pamphlet, embodying the circuit, etc., is supplied by this firm. In recent years more compact, but necessarily less accurate, instruments have been introduced (see Section I, 53D); these embody a thermionic valve potentiometer, are generally of the portable type, and are claimed to give an accuracy of about 0·02 *p*H units. Very rugged glass, calomel, and other electrodes have been developed for use with these portable instruments; these are shown in photograph at bottom of Plate I.

I, 53. Experimental details concerning potentiometric titrations.—A. Neutralisation reactions. The simplest apparatus consists of a beaker containing the base and into which is immersed a hydrogen or glass electrode, the apparatus being connected as shown in Fig. 1-20. A burette containing the acid is clamped immediately above the beaker, and some form of mechanical stirring is provided for the solution. If the quinhydrone electrode is to be used, the acid is placed in the beaker and the base in the burette. The e.m.f. of the cell containing the initial solution is determined, and then the measurement is repeated at intervals of 2 ml. addition from the burette. When the e.m.f. changes somewhat more rapidly as the end point is approached, the e.m.f. readings are taken at more frequent intervals, and eventually after each drop. After the first rough titration, the exact procedure will be apparent. Draw a curve with the e.m.f. readings (or *p*H) as ordinates and the burette readings as abscissae : the end point of the break in the curve determines the equivalence point. A more satisfactory determination of the end point is obtained by the differential method, in which the change of e.m.f. (or *p*H) per unit of titrant is the ordinate. If we plot the change of potential in milli-volts caused by 0·1 ml. increments of the reagent ($\Delta E/\Delta V$) against the volume of the titrant corresponding to the middle of the titration interval (here the burette reading + 0·05 ml.), a curve of the type shown in Fig. 1-22 is obtained. The abscissa corresponding to the maximum gives the end point of the reaction with sufficient accuracy for all ordinary purposes. It is possible by means of the *differential method of potentiometric titration*, introduced by D. C. Cox in 1925 and subsequently improved by D. A. MacInnes, to obtain values of $\Delta E/\Delta V$ directly and

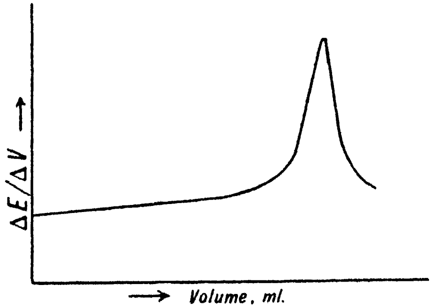

FIG. 1-22.

thus to considerably increase the accuracy of the determination of the end point.*

The accuracy with which the end point can be found potentiometrically depends upon the magnitude of the change in e.m.f. in the neighbourhood of the equivalence point, and this depends upon the concentration and the strength of the acid and alkali (compare Sections **I, 33-36**). Satisfactory results are obtained in all cases except (*a*) those in which either the acid or the base is very weak ($K < 10^{-8}$) and the solutions are dilute, and (*b*) those in which both the acid and the base are weak. In the latter case an accuracy of about 1 per cent may be obtained in $0{\cdot}1N$ solution.

The method may be used to titrate a mixture of acids which differ greatly in their strengths, *e.g.*, acetic and hydrochloric acids ; the first break in the titration curve occurs when the stronger of the two acids is neutralised, and the second when neutralisation is complete. For this method to be successful, the two acids or bases should differ in strength by at least 10^5 to 1.

B. Oxidation-reduction reactions.—The apparatus employed here is similar to that for neutralisation reactions. The beaker contains the reducing agent, appropriately acidified, if necessary, and also a calomel electrode and a bright platinum electrode, similar to that used with the quinhydrone electrode (Section **I, 52B**). The burette will contain the oxidising agent. The experimental details, including the determination of the end point, are identical with those already given.

Numerous oxidation-reduction titrations can be carried out in this manner. A few typical ones are enumerated below.†

Potassium permanganate (*acid*) with ferrous iron, oxalate (at 70°C), ferrocyanide, iodide, nitrite, stannous tin, thallous thallium, and titanous titanium.

Potassium dichromate (*acid*) with ferrous iron, ferrocyanide, iodide (in HCl), antimonious antimony, arsenious arsenic, stannous tin, and titanous titanium.

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* See, for example, D. A. MacInnes, *The Principles of Electrochemistry*, p. 306 (Rheinold Publishing Corporation, 1939) ; W. W. Scott-N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. II, p. 2318 (1939).

† For further details, see Kolthoff and Furman, *Potentiometric Titrations*, 1931 (J. Wiley and Co.).

Ceric sulphate with ferrous iron, oxalate (catalyst present), ferrocyanide, arsenious arsenic, antimonious antimony, stannous tin, hydrogen peroxide, nitrite, mercurous mercury, thallous thallium, titanous titanium, tellurite, vanadyl salts and uranyl salts.

Iodine with thiosulphate, copper salts in the presence of acetic acid, and arsenites in the presence of bicarbonate.

Titanous chloride or sulphate with ferric iron, antimonate, ferricyanide, mercuric mercury, stannic tin, titanic titanium, and uranyl salts (55–60°C).

C. Precipitation reactions. Here one electrode may be a saturated calomel or, less conveniently, a hydrogen electrode, and the other must consist of one which will readily come into equilibrium with one of the ions of the precipitate. For example, in the titration of silver ions with a halogen (chloride, bromide or iodide) this must be a silver electrode. It may consist of a silver wire, or of a platinum wire or gauze plated with silver* and sealed into a glass tube. Since a halide is to be determined, the salt bridge must be a saturated solution of potassium nitrate. Excellent results are obtained by titrating silver nitrate solution with thiocyanate ions.

RECENT DEVELOPMENTS IN THE TECHNIQUE OF POTENTIOMETRIC TITRATION AND OF OTHER PHYSICAL METHODS OF ANALYSIS.

D. Potentiometric Titration. The use of the troublesome reference electrode and salt bridge was first eliminated through the development of the polarised mono-metallic system and of the bi-metallic self-polarising system. The former consists of two pure platinum wires, one polarised anodically and the other cathodically with a polarising current of $0{\cdot}5 \times 10^{-5}$ ampere (Willard and Fenwick, 1922). Such a system gives a sharp break of potential at the end point of many, particularly oxidation-reduction, titrations. This is due to the difference in the degree of reversibility of the electrode reaction before and after the end point. The action of bi-metallic systems will be readily understood from the following discussion.

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* This is most conveniently carried out by immersing the platinum in $0{\cdot}1N$ silver nitrate to which enough potassium cyanide has been added just to dissolve the precipitate initially formed. Electrolyse the solution of potassium argentocyanide, using the platinum to be plated as the cathode and a platinum wire as anode. A 6-volt accumulator in series with a variable resistance may be used, and the current adjusted to about 0·05 ampere. The plating is continued for about 15 to 20 minutes when a fairly thick deposit of silver should be formed. The electrode must be thoroughly washed to remove all traces of cyanide.

It has been found that certain metals and non-metals, *e.g.*, natural graphite, carborundum, silicon, cadmium, nickel, cobalt, and copper, acquire a more or less definite potential when immersed in solutions, and that these do not change appreciably as the *p*H of the solution in which they are placed is altered. On the other hand elements, such as platinum, antimony and tungsten, adjust themselves more or less in a regular manner as the *p*H of the solution in which they are immersed is varied. If one of the former type of electrode is combined with one of the latter, then there is a small difference of potential between them when they are placed in, say, an acid solution which is to be titrated. During the progress of the titration there is little change in the e.m.f. of the cell, but at the end point the potential of one electrode changes rapidly whereas that of the other remains approximately constant. Thus there is a sudden change of e.m.f. at the equivalence point. For oxidation-reduction titrations it has been shown that palladium and other metals of its family in the periodic system (but excluding platinum) and also tungsten do not change appreciably in potential as the concentrations of the oxidant and reductant are varied. The most useful electrode pair for this purpose is platinum-tungsten. The potential of the former responds readily to changes in concentration of the oxidant and reductant, but that of the latter does not : at the end of the titration there is a large increase in the e.m.f. of the Pt-W cell.

Subsequent improvements have led to the elimination of the potentiometer, of the tapping key, and of the storage battery. This was rendered possible by the use of thermionic valves ; the current drawn from the titration cell can be amplified without polarisation. The "**thermionic titrimeter without batteries**" of Willard and Hager* (1936) is of this type ; it employs a Weston micro-ammeter as the indicating instrument. G. F. Smith (1936) has designed a similar apparatus which, however, replaces the sluggish, fragile and expensive micro-ammeter by a small cathode-ray tube (" magic eye "), which is inexpensive and highly sensitive. He terms the

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* This apparatus is marketed by E. H. Sargent and Company, 155 East Superior Street, Chicago, U.S.A.

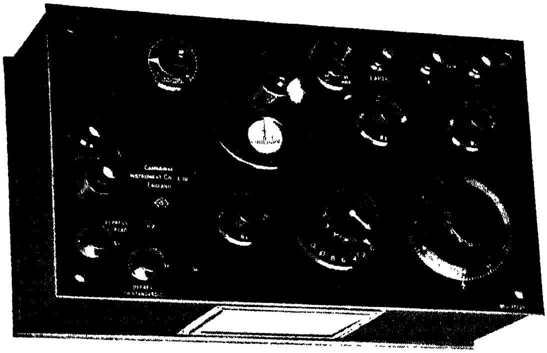


FIG. 1–23

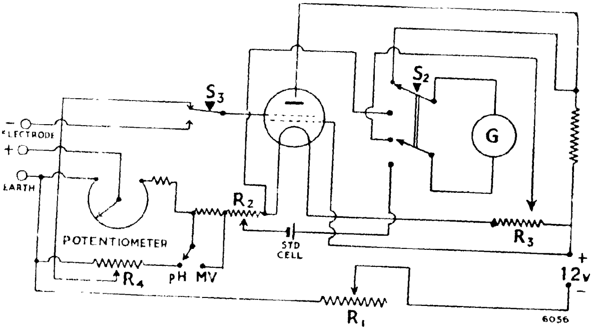
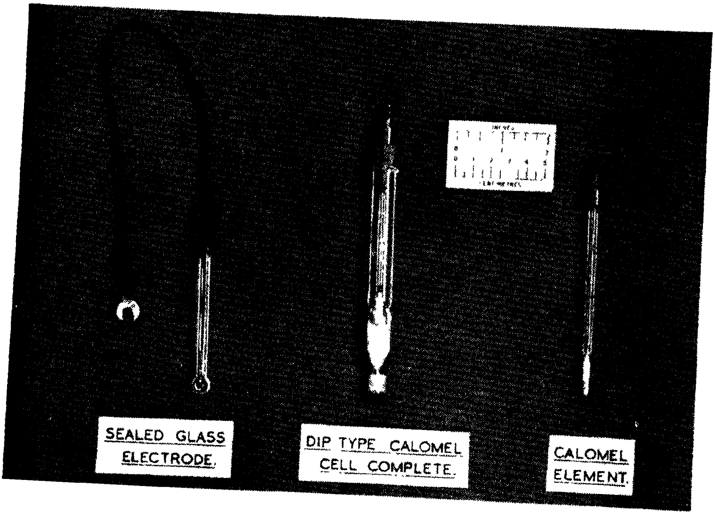


FIG. 1–24



apparatus a "**sectrometer**"* ; this will doubtless find very wide application when its properties and advantages are fully realised. The apparatus is placed along the side of the titration vessel, and its effect is somewhat comparable to the use of a colour indicator ; the only differences are a greater warning of the approaching end point and the instantaneous response of the cathode ray tube. A wink of the "magic eye" indicates the completeness of the reaction.

It must, however, be pointed out that the first real advance in potentiometric technique was made by K. H. Goode in 1922, who replaced the usual potentiometer by a thermionic valve and thus introduced what are now commonly termed **thermionic valve potentiometers.**† Numerous improvements have subsequently been made, chiefly with the object of utilising the glass electrode. An excellent commercial instrument is the Cambridge *p*H meter‡ ; the instrument itself is shown in Fig. 1-23, and the circuit and connexion in Fig. 1-24 (see Plate I). The instrument may be employed with the glass, hydrogen, quinhydrone, and antimony electrodes, and readings may be obtained either directly in *p*H units (with the glass electrode and to within 0·01–0·02 *p*H units) or in millivolts (to within 0·001–0·002 volts); it can also be adapted for redox and precipitation titrations. For further particulars, the reader is referred to the pamphlets supplied by the manufacturers.

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* The complete "sectrometer," including electrodes, is supplied by the G. F. Smith Chemical Co., of 867 McKinley Avenue, Columbus, Ohio, U.S.A. The agents for Great Britain are F. W. Berk and Co. Ltd., 52-54 Leadenhall Street, London, E.C.3, England. The apparatus is designed for use on 110 volts and 60 cycles A.C., but by connecting a 25 watt 110 volt lamp in series with the sectrometer circuit it may be employed with 220/240 volts 50 cycles mains. A very comprehensive booklet entitled "The Electron Beam Sectrometer for Potentiometric Tritrations" is available.

The Fisher Scientific Company of 711–723 Forbes Street, Pittsburgh, Pa., U.S.A., market what they call the "Fisher titrimeter." This somewhat elaborate apparatus also incorporates the "magic eye" as indicator, and may be used for acid-base, oxidation-reduction, and conductivity titrations, and also for measurements of D.C. voltage and resistance. It is, of necessity, more expensive than the Smith "sectrometer".

† For further details, see, for example, S. Glasstone, *Electrometric Methods in Physical and Analytical Chemistry* (Institute of Chemistry, London, 1934) ; H. T. S. Britton, *Hydrogen Ions*, 2nd Edn., p. 133 (Chapman and Hall, 1932) ; N. A. McKenna, *Theoretical Electrochemistry*, p. 41 (Macmillan, 1939) ; W. W. Scott-N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. II, p. 2321 (Van Nostrand—The Technical Press, 1939).

‡ Figs. 1-23 and 1-24 are reproduced by courtesy of the Cambridge Instrument Co. Ltd., of 13 Grosvenor Place, London, S.W.1, England. This firm also supplies a Cambridge Portable *p*H Meter, which is self-contained but in other respects is similar to the above. Numerous other *p*H meters are marketed ; these include : the Portable Universal *p*H Indicator (Leeds and Northrup Co., Philadelphia, Pa., U.S.A. and Integra Co. Ltd., Birmingham), the Beckman *p*H Meter (Eimer and Amend, New York, U.S.A., and Griffin and Tatlock Ltd., London) ; the Coleman *p*H Electrometer (Coleman Electric Co., Maywood, Ill., U.S.A., and Baird and Tatlock (London) Ltd., London) ; Hellige *p*H Meter (Hellige Inc., Long Island City, N.Y., U.S.A., and A. Gallenkamp and Co. Ltd., London). Suitable glass and calomel electrodes are supplied *inter alia* by the Cambridge Instrument Co., and are shown at bottom of Plate I.

E. Conductometric titrations. A discussion of this method, which depends upon the measurement of the electrical conductivity of the solution after successive additions of the reagent, is outside the scope of this book. The reader is referred to the various special monographs devoted to the subject.* Mention must, however, be made of the fact that the cathode ray tube ("magic eye") has been incorporated in a commercial apparatus† for the rapid and comparatively accurate measurement of the conductivity of solutions; this is particularly useful for conductometric titrations.

F. Spectroscopic methods. Methods of quantitative analysis dependent upon the use of spectroscopy are finding increasing application, particularly in metallurgical analysis. Their great disadvantage is that an expensive equipment is required, but when once this has been obtained results can, in many cases, be obtained with comparative rapidity.‡

G. Polarographic methods. By applying a steadily increasing e.m.f. to an electrolytic cell with a dropping mercury cathode and a stationary mercury anode (the latter is covered by the solution to be analysed) and utilising a device whereby the current and voltage are measured and automatically recorded on a revolving drum, current voltage curves may be obtained. Such an instrument is termed a **polarograph** and the corresponding current-voltage diagram is called a **polarogram.** When the solution contains a substance which can be reduced, *e.g.*, a metallic ion or any other oxidising agent (inorganic or organic), a sudden increase in current is observed at the voltage at which reduction occurs (decomposition voltage, see Section **I, 65**) ; this voltage is more or less characteristic of the substance being reduced (reduction potential). After the decomposition potential has been attained, the current increases rapidly until a final (or saturation) value is reached, the latter being related to the concentration of the substance being reduced. If a number of metallic ions or oxidising agents are present and the respective reduction potentials differ by more than 0·2 volt, it is possible to determine the concentration of each in one experiment. This forms the basis of the use of the polarograph in quantitative analysis.

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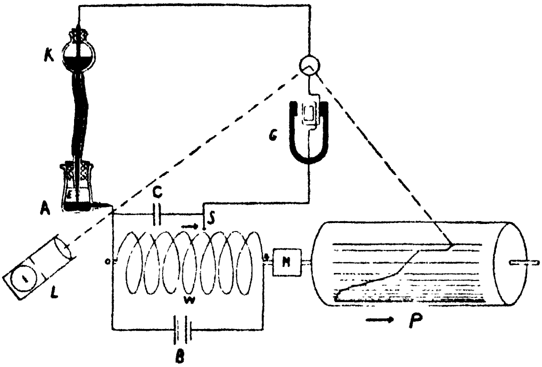
* See, for example, H. T. S. Britton, *Conductometric Titrations*, 1934 (Chapman and Hall).

† This is termed the "Mullard Measuring Bridge, Type GM. 4140" and is manufactured by the Mullard Wireless Service Co. Ltd., of 225 Tottenham Court Road, London, W.1, England.

‡ For further details see, for example, *Thorpe's Dictionary of Applied Chemistry*, Volume II, p. 688 (Longmans, Green and Co., 1938); A. C. Candler, *Spectographic Analysis in Great Britain* (Adam Hilger, 1939); W. R. Brode, *Spectrographic Analysis* in Scott-Furman, Standard Methods of Chemical Analysis, Vol. II, p. 2592 (1939).

The instrument has been developed chiefly by J. Heyrovsky and his co-workers (1925 →). Its use will be evident from Fig. 1-25. The solution to be analysed is contained in a small electrolytic vessel above a layer of mercury **A**, which serves as anode. The dropping mercury cathode is shown at **K** ; small drops of mercury, fed from an adjustable storage vessel, are discharged slowly from a fine glass capillary into the electrolyte. The surface of the dropping cathode is thus constantly renewed, and hence the conditions under which reduction takes place are readily reproducible. The potential across the cell is slowly increased by means of a precision rotating potentiometer **W** which is directly geared to the recording drum **P** around which is wrapped a piece of photographic paper. The current flowing through the cell is recorded on the drum by a spot of light from the mirror of the galvanometer **G**, the sensitivity of which can be accurately varied between 1 and 10,000 by means of a switch ; the



A. = mercury anode overlaid by
E = the solution under test
K = the dropping mercury cathode
B = Source of current (storage battery)
W = potentiometer wire coil
S = sliding contact
M = motor
P = polarogram
G = moving coil reflecting galvanometer
L = illuminating lamp
C = condenser

FIG. 1-25. Recording the course of electrolysis with a dropping mercury cathode.

galvanometer is connected in series with the cell through the condenser **C**.

No current is passed by the cell until the deposition or reduction potential of one of the substances present in solution is reached. A sharp increase in current then sets in, *i.e.*, the mercury-water interface becomes denuded of reducible material by electrolysis, and further electrolysis is limited by the rate at which fresh material diffuses to the interface from the main bulk of the solution. Further increase in the voltage results in no further increase in current until the next deposition potential is reached, when the phenomenon is repeated. In this way a curve (polarogram) consisting of a series of steps is obtained : the voltage at which a step occurs indicates qualitatively the substance responsible and the height of the step (under controlled conditions) its concentration. A typical polarogram (recorded twice to indicate its reproducibility) is shown in Fig. 1-26.

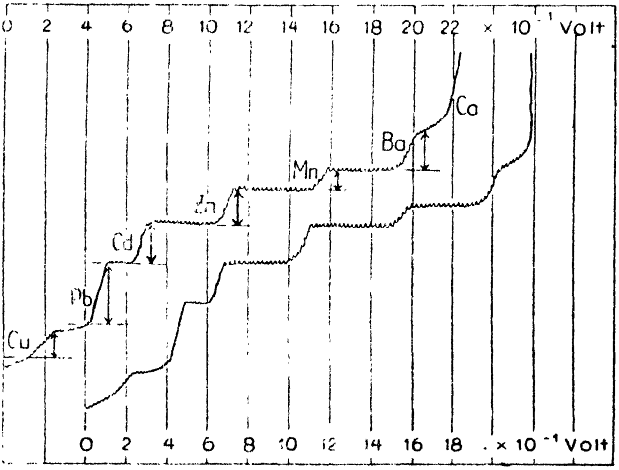


FIG. 1-26. Polarogram of a solution of various metallic chlorides.

Determinations can be made in faintly acid (*p*H $\nless$ 3·5), neutral or alkaline solutions. With the exception of magnesium, all the common cations may be detected and determined in this way. When two or more substances with the same or but slightly different decomposition potentials are present together, separation may be achieved by the addition of a complex-forming reagent, such as potassium cyanide or ammonium oxalate ; the resulting complex ions frequently have deposition potentials differing from one another and from those of the free ions. The method may also be applied to the determination of chromates, iodates, bromates, chlorates, nitrates, nitrites, dissolved oxygen, dissolved sulphur dioxide, dissolved nitric oxide, hydrogen peroxide, organic nitro compounds, azo compounds, aldehydes, ketones, unsaturated acids, etc. For further details, the reader is referred to the literature on the subject.* The great disvantage of this apparatus is that its cost is very high.

H. Methods based upon the use of X-rays, electron diffraction, Raman and absorption spectra. The reader is referred to the summary in the *Annual Reports of the Chemical Society*, 1939, **35**, 381-398.

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* See, especially, reviews by J. Heyrovsky in W. Böttger, *Physikalische Methoden der chemischen Analyse*, Vol. II (Akad. Verlag. Leipzig, 1938) and by I. M. Kolthoff and J. I. Lingane, *The Fundamental Principles and Applications of Electrolysis with the Dropping Mercury Electrode and Heyrovsky's Polarographic Method of Analysis* (Chemical Reviews, 1939, **24**, 1-95).

W. Edwards and Co., of Vaughan Road, London, S.E.5, England, market an excellent model of the polarograph, and issue a pamphlet which contains much valuable information and many literature references. Figs. 1-25 and 1-26 are reproduced by courtesy of this firm.

An inexpensive apparatus incorporating the dropping mercury electrode system (the Fisher " electrodropode ") is marketed by the Fisher Scientific Co., of Pittsburgh, U.S.A.

THEORY OF GRAVIMETRIC ANALYSIS

I, 54. Gravimetric analysis.—Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. The element or compound is separated from a weighed portion of the substance being examined. A large proportion of the determinations of gravimetric analysis is concerned with the transformation of the element or radical to be determined into a pure stable compound, which can be readily converted into a form suitable for weighing. The weight of the element or radical may then be readily calculated from a knowledge of the formula of the compound and the atomic weights of the constituent elements.

The separation of the element or of the compound containing it may be effected in a number of ways, the most important of which are: (*a*) precipitation methods, (*b*) volatilisation or evolution methods, (*c*) electro-analytical methods, and (*d*) miscellaneous physical methods. It is proposed to utilise these four as the basis for the classification of gravimetric methods, and to discuss the theory of each in turn.

It may be mentioned at this stage that the great advantage of gravimetric over volumetric analysis is that the constituent may be seen and examined for the presence of impurities and a correction applied, if necessary; their disadvantage is that they are generally more time-consuming.

I, 55. PRECIPITATION METHODS

These are perhaps the most important with which we are concerned in gravimetric analysis. The constituent being determined is precipitated from solution in a form which is so slightly soluble that no appreciable loss occurs when the precipitate is separated by filtration and weighed. Thus in the determination of silver, a solution of the substance is treated with an excess of sodium or potassium chloride solution, the precipitate is filtered off, well washed to remove soluble salts, dried at 130–150°C, and weighed as silver chloride. Frequently the constituent being estimated is weighed in a form other than that in which it was precipitated. Thus magnesium is precipitated as magnesium ammonium phosphate $Mg(NH_4)PO_4, 6H_2O$, but is weighed, after ignition, as the pyrophosphate $Mg_2P_2O_7$. The following Table contains the forms in which the compounds of the common elements are usually weighed: this includes the electro-analytical methods discussed in Section **I, 64** *et seq.*

TABLE XVII. FORMS IN WHICH ELEMENTS AND RADICALS ARE COMMONLY PRECIPITATED AND WEIGHED IN GRAVIMETRIC ANALYSIS.

Element	*Precipitated as*	*Weighed as*
Pb	*1*. $PbSO_4$; *2*. $PbCrO_4$; *3*. $PbMoO_4$; *4*. PbO_2.	*1*. $PbSO_4$; *2*. $PbCrO_4$; *3*. $PbMoO_4$; *4*. PbO_2.*
Ag	*1*. AgCl; *2*. Ag.	*1*. AgCl; *2*. Ag.*
Hg	*1*. HgS; *2*. Hg zinc thiocyanate; *3*. Cu ethylenediamine mercuri-iodide.	*1*. HgS; *2*. $Hg[Zn(CNS)_4]$; *3*. $[Cu\ en_2]\ [HgI_4]$.
Bi	*1*. BiOI; *2*. Bi pyrogallate; *3*. Bi cupferron complex; *4*. Bi "oxinate," H_2O.	*1*. BiOI; *2*. $Bi(C_6H_3O_3)$; *3*. Bi_2O_3; *4*. $Bi(C_9H_6ON)_3$.
Cd	*1*. $CdMoO_4$; *2*. Cd β-naphtha-quinoline complex; *3*. Cd quinaldinate; *4*. Cd pyridine thiocyanate; *5*. Cd.	*1*. $CdMoO_4$; *2*. $[(C_{13}H_9N)_2H_2]\ (CdI_4)$; *3*. $Cd(C_{10}H_6NO_2)_2$; *4*. $[Cd(C_5H_5N)_2](CNS)_2$; *5*. Cd.*
Cu	*1*. $Cu_2(CNS)_2$; *2*. Cu benzoinoxime; *3*. Cu salicylaldoxime; 4. Cu quinaldinate; *5*. Cu pyridine thiocyanate; *6*. Cu ethylenediamine mercuri-iodide; *7*. Cu.	*1*. $Cu_2(CNS)_2$; *2*. $Cu(C_{14}H_{11}O_2N)$; *3*. $Cu(C_7H_6O_2N)_2$; *4*. $Cu(C_{10}H_6NO_2)_2$, H_2O; *5*. $[Cu(C_5H_5N)_2](CNS)_2$; *6*. $[Cu\ en_2]\ [Hg]I_4]$; 7. Cu.*
As	*1*. As_2S_3; *2*. $Mg(NH_4)AsO_4$, $6H_2O$; *3*. $NH_4UO_2AsO_4$, xH_2O.	*1*. As_2S_3; *2*. $Mg(NH_4)AsO_4$, $6H_2O$ or as $Mg_2As_2O_7$; *3*. U_3O_8.
Sb	*1*. Sb_2S_3; *2*. Sb pyrogallate.	*1*. Sb_2S_3 or Sb_2O_4; *2*. $Sb(C_6H_5O_4)$.
Sn	*1*. SnO_2, xH_2O; *2*. Sn cupferron complex; *3*. Sn phenylarsonate.	*1*. SnO_2; *2*. SnO_2; *3*. SnO_2.
Mo.	*1*. $PbMoO_4$; *2*. Mo benzoinoxime; *3*. Mo "oxinate."	*1*. $PbMoO_4$; *2*. MoO_3; *3*. $MoO_2(C_9H_6ON)_2$.
Se	*1*. Se.	*1*. Se.
Te	*1*. Te; *2*. TeO_2.	*1*. Te; *2*. Te.
Pt	*1*. Pt; *2*. $(NH_4)_2[PtCl_6]$.	1. Pt; *2*. Pt.
Pd	*1*. $Pd(CN)_2$; *2*. Pd dimethylglyoxime; *3*. Pd α-nitroso-β-naphtholate; *4*. Pd α-nitro-β-naphtholate.	*1*. Pd; *2*. $Pd(C_4H_7O_2N_2)_2$; *3*. $Pd(C_{10}H_6O_2N)_2$; *4*. $Pd(C_{10}H_6O_3N)_2$.
Au	*1*. Au.	*1*. Au.

* Those elements (and PbO_2) marked with an asterisk are electrolytic determinations.

TABLE XVII—*continued.*

Element	*Precipitated as*	*Weighed as*
Al	*1.* $Al(OH)_3$; *2.* Basic Al succinate ; *3.* Al " oxinate."	*1.* Al_2O_3 ; *2.* Al_2O_3 ; *3.* $Al(C_9H_6ON)_3$.
Be	*1.* $Be(OH)_2$.	*1.* BeO.
Cr	*1.* $Cr(OH)_3$; *2.* Hg_2CrO_4; *3.* $BaCrO_4$.	*1.* Cr_2O_3 ; *2.* Cr_2O_3 ; *3.* $BaCrO_4$.
Fe	*1.* $Fe(OH)_3$; *2.* Fe cupferron complex.	*1.* Fe_2O_3 ; *2.* Fe_2O_3.
Ni	*1.* Ni dimethylglyoxime; *2.* Ni salicylaldoxime ; *3.* Ni pyridine thiocyanate ; *4.* Ni α-benzil-dioxime ; *5.* Ni.	*1.* $Ni(C_4H_7O_2N_2)_2$; *2.* $Ni(C_7H_6O_2N)_2$; *3.* $[Ni(C_5H_5N)_4](CNS)_2$; *4.* $Ni(C_{14}H_{11}O_2N_2)_2$; *5.* Ni.*
Co	*1.* Co α-nitroso-β-naphtholate ; *2.* Co α-nitro-β-naphtholate; *3.* Co phenylthiohydantoate complex ; *4.* Co pyridine thiocyanate ; *5.* Co.	*1.* $Co(C_{10}H_6O_2N)_3,2H_2O$; *2.* $Co(C_{10}H_6O_3N)_3$; *3.* Co_3O_4 (impure) and then as *1*, *2*, *4* or *5* ; *4.* $[Co(C_5H_5N)_4](CNS)_2$; *5.* Co.*
Zn	*1.* $Zn(NH_4)PO_4,6H_2O$; *2.* ZnS ; *3.* Zn quinaldinate ; *4.* Zn pyridine thiocyanate ; *5.* Zn.	*1.* $Zn(NH_4)PO_4$ or as $Zn_2P_2O_7$; *2.* ZnS or as *1* ; *3.* $Zn(C_{10}H_6O_2N)_2,2H_2O$; *4.* $[Zn(C_5H_5N)_2](CNS)_2$; *5.* Zn.*
Mn	*1.* $Mn(NH_4)PO_4,H_2O$.	*1.* $Mn_2P_2O_7$ or as $Mn(NH_4)PO_4, H_2O$.
V	*1.* Hg_3VO_4 ; *2.* Ag_3VO_4.	*1.* V_2O_5 ; *2.* Ag_3VO_4.
U (UO_2)	*1.* $(NH_4)_2U_2O_7$; *2.* U " oxinate."	*1.* U_3O_8 ; *2.* $UO_2(C_9H_6ON)_2, C_9HO_7N$.
Th	*1.* $Th(C_2O_4)_2$; *2.* Th sebacate.	*1.* ThO_2 ; *2.* ThO_2.
Ce	*1.* $Ce(IO_3)_4$.	*1.* CeO_2.
Ti	*1.* Ti " oxinate " ; *2.* $TiO(OH)_2$ with tannin and antipyrine ; *3.* $TiO(OH)_2$ with selenious acid ; *4.* Ti para-hydroxy-phenylarsonate.	*1.* $TiO(C_9H_6ON)_2$; *2.* TiO_2 ; *3.* TiO_2 ; *4* TiO_2.
Zr	*1.* $ZrH_2(PO_4)_2$; *2.* basic Zr selenite ; *3.* Zr *n*-propylarsonate ; *4.* Zr para-hydroxy-phenylarsonate.	*1.* $Zr_2P_2O_7$; *2.* ZrO_2 ; *3.* ZrO_2 ; *4.* ZrO_2.
Tl	*1.* Tl_2CrO_4 ; *2.* $Tl_3[Co(NO_2)_6]$.	*1.* Tl_2CrO_4 ; *2.* $Tl_3[Co(NO_2)_6]$.
Ca	*1.* CaC_2O_4,H_2O ; *2.* $CaCO_3$; *3.* CaO.	*1.* CaC_2O_4,H_2O ; *2.* $CaCO_3$; *3.* CaO.

TABLE XVII—*continued.*

Element	*Precipitated as*	*Weighed as*
Sr	1. $SrSO_4$; 2. SrC_2O_4,H_2O.	1. $SrSO_4$; 2. SrO.
Ba	1. $BaSO_4$; 2. $BaCrO_4$.	1. $BaSO_4$; 2. $BaCrO_4$.
Mg	1. Mg " oxinate " ; 2. $Mg(NH_4)PO_4,6H_2O$.	1. $Mg(C_9H_6ON)_2$; 2. $Mg(NH_4)PO_4,6H_2O$ or as $Mg_2P_2O_7$.
Na	1. Na_2SO_4 ; 2. Na zinc uranyl acetate ; 3. Na magnesium uranyl acetate.	1. Na_2SO_4 ; 2. $NaZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$, 3. $NaMg(UO_2)_3(C_2H_3O_2)_9$, 6·5 H_2O.
K	1. $K_2[PtCl_6]$; 2. $KClO_4$; 3. K_2SO_4 ; 4. $K_2Na[Co(NO_2)_6]$, H_2O.	1. $K_2[PtCl_6]$; 2. $KClO_4$; 3. K_2SO_4 ; 4. $K_2Na[Co(NO_2)_6]$, H_2O.
Li	1. Li_2SO_4 ; 2. by extraction as LiCl.	1. Li_2SO_4 ; 2. LiCl.
NH_4^+	1 $(NH_4)_2[PtCl_6]$.	1. $(NH_4)_2[PtCl_6]$.
W	1. Benzidine tungstate ; 2. Tannin-antipyrine-tungstate complex ; 3. Tungstyl " oxinate."	1. WO_3 ; 2. WO_3 ; 3. $WO_2(C_9H_6ON)_2$
Anions		
Cl^-,Br^-	1. AgCl, AgBr.	1. AgCl, AgBr.
I^-	1. AgI ; 2. PdI_2.	1. AgI ; 2. PdI_2.
CNS^-	1. AgCNS ; 2. $Cu_2(CNS)_2$; 3. $BaSO_4$.	1. AgCNS ; 2. $Cu_2(CNS)_2$; 3. $BaSO_4$.
CN^-	1. AgCN.	1. AgCN.
F^-	1. PbClF ; 2. CaF_2; 3. $(C_6H_5)_3SnF$.	1. PbClF ; 2. CaF_2; 3. $(C_6H_5)_3SnF$.
ClO_3^-	1. AgCl.	1. AgCl.
ClO_4^-	1. AgCl ; 2. $KClO_4$.	1. AgCl ; 2. $KClO_4$.
SO_4^{--}, S^{--}, SO_3^{--}, $S_2O_3^{--}$	1. $BaSO_4$.	1. $BaSO_4$.
PO_4^{---}	1. $Mg(NH_4)PO_4,6H_2O$; 2. $(NH_4)_3PO_4,12MoO_3$, $2HNO_3,H_2O$	1. $Mg_2P_2O_7$; 2. $P_2O_5,24MoO_3$.
HPO_3^{--} $H_2PO_2^-$	1. Hg_2Cl_2 ; 2. $Mg(NH_4)PO_4,6H_2O$.	1. Hg_2Cl_2 ; 2. $Mg_2P_2O_7$.
$C_2O_4^{--}$	1. CaC_2O_4,H_2O.	1. CaC_2O_4,H_2O or $CaCO_3$ or CaO.
SiO_3^{--}, SiF_6^{--}	1. SiO_2,xH_2O.	1. SiO_2.
NO_3^-	1. Nitron nitrate.	1. $C_{20}H_{16}N_4,HNO_3$.

The factors which determine a successful analysis by precipitation are:

(*A*) The precipitate must be so sparingly soluble that the precipitation may be made quantitative. In practice this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance, *viz.*, 0·1 mg.

(*B*) The physical nature of the precipitate must be such that it can be readily separated from the solution by filtration, and can be washed free of soluble impurities. These conditions require that the particles are of such size that they do not pass through the filtering medium, and that the particle size is unaffected (or, at least, not diminished) by the washing process.

(*C*) The precipitate must be convertible into a pure substance of definite chemical composition; this may be effected either by ignition or by a simple chemical operation, such as evaporation, with a suitable liquid.

Factor (*A*), which is concerned with the completeness of precipitation has already been dealt with in connexion with the solubility product principle (Sections **I, 8** and **9**). Therein are discussed the influence upon the solubility of the precipitate of a salt with a common ion, of salts with no common ion, of acids and bases, and of temperature.

It was assumed throughout that the compound which separated out from the solution was chemically pure, but this is not always the case. The purity of the precipitate depends *inter alia* upon the substances present in solution both before and after the addition of the reagent, and also upon the exact experimental conditions of precipitation. In order to understand the influence of these and other factors, it will be necessary to give a short account of the properties of colloids.

I, 56. The colloidal state.—The colloidal state of matter is distinguished by a certain range of particle size, as a consequence of which certain characteristic properties become apparent. Before discussing these, mention must be made of the various units which are employed in expressing small quantities. The most important of these are:

$1\mu = 10^{-3}$ mm. $\qquad$ $1\ m\mu = 1\mu\mu = 10^{-6}$ mm.

1 Angstrom unit $= 1\text{Å} = 10^{-10}$ metre $= 10^{-7}$ mm. $= 0{\cdot}1\ m\mu$.

Colloidal properties are, in general, exhibited by substances of particle size ranging between 0·1μ and 1 mμ. Ordinary quantitative filter paper will retain particles up to a diameter of about 10^{-2} mm. or 10μ, so that colloidal solutions in this respect behave like true solutions (size of molecules is of the order of 0·1 mμ or 10^{-8} cm.). The limit of vision under the microscope is about 0·2μ. If a powerful beam of light is passed through a colloidal solution and the solution is viewed at right angles to the incident light, a scattering of light is observed. This is the so-called **Tyndall effect.** True solutions, *i.e.*, those with particles of molecular dimensions, do not exhibit a Tyndall effect, and are said to be " optically empty." Use is made of the Tyndall effect in the ultra-microscope ; here the Tyndall cone or beam is observed in a microscope which is situated at right angles to the path of the incident light. The diffraction images are thus seen, and it is possible to observe the light scattered by each particle separately. The limit of visibility under the ultra-microscope is about 10 mμ.

By the use of X-rays the nature of the smallest unit of colloidal substances may be ascertained. It has been found that most substances consist of minute crystalline particles ; a few, such as silica and stannic oxide are amorphous. An intermediate stage is also possible : a gradual development of crystalline particles may occur with some amorphous substances upon " ageing " or with suitable treatment, such as hot digestion with water or electrolytic solutions (Section **I, 58**).

An important consequence of the smallness of the size of the particles is that the ratio of surface to weight is extremely large. Phenomena which depend upon the size of the surface, such as adsorption, will therefore play an important part with substances in the colloidal state. Table XVIII clearly shows the influence of particle size in connexion with a one centimetre cube decimally divided.

The characteristic properties of colloidal particles are :—

(*a*) They exhibit a Tyndall effect when viewed with proper illumination.

(*b*) They may be separated from true solutions of substances by means of a collodion or parchment membrane, *i.e.*, by the process of dialysis.

(*c*) They may be regarded as possessing electrical charges since they migrate under the influence of a suitable potential gradient.

TABLE XVIII. INCREASE IN NUMBER AND TOTAL SURFACE OF PARTICLES AS A ONE CENTIMETRE CUBE IS DECIMALLY DIVIDED.

Number of particles	*Length of edge in cm.*	*Total surface in sq. cm.*
1	1	6
10^6	10^{-2}	6×10^2
10^{12}	10^{-4} (= 1μ)	6×10^4
10^{15}	10^{-5}	6×10^5
10^{21}	10^{-7} (= 1mμ)	6×10^7 (= 1·48 acres)
10^{24}	10^{-8} (= 1Å)	6×10^8

For convenience, we may divide colloids into two main groups, designated as **suspensoids** and **emulsoids.*** The chief properties of each class are summarised in the following table, although, it must be emphasised, that the distinction is not an absolute one, since some gelatinous precipitates (*e.g.*, aluminium and other metallic hydroxides) have properties intermediate between those of suspensoids and emulsoids.

Suspensoids (or Lyophobic Colloids)	*Emulsoids* (or Lyophilic Colloids)
1. The solutions (or *sols*) are only slightly viscous. Examples: sols of metals, silver halides, metallic sulphides, etc.	1. The solutions are very viscous; they set to jelly-like masses known as *gels*. Examples: sols of silicic acid, stannic oxide, gelatin.
2. A comparatively minute concentration of an electrolyte results in flocculation. The change is, in general, irreversible; water has no effect upon the flocculant.	2. Comparatively large concentrations of electrolytes are required to cause precipitation ("salting out"). The change is, in general, reversible, and is effected by the addition of a solvent (water).
3. Suspensoids, ordinarily, have an electric charge of definite sign, which can be changed only by special methods.	3. Most emulsoids change their charge readily, *e.g.*, they are positively charged in acid medium and negatively charged in an alkaline medium.
4. The ultra-microscope reveals bright particles in vigorous motion (Brownian movement).	4. Only a diffuse light cone is exhibited under the ultra-microscope.

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* For a detailed account, see H. Kruyt, *Colloids*, 1930 (Chapman and Hall).

The process of dispersing a gel or a flocculated solid to form a sol is called **peptisation.**

The stability of colloidal solutions is intimately associated with the electrical charge on the particles. Thus in the formation of an arsenious sulphide sol by precipitation with hydrogen sulphide in acid solution, sulphide ions are primarily adsorbed (since every precipitate has a tendency to adsorb its own ions), and in order to maintain the electro-neutrality of the solution, an equivalent quantity of hydrogen ions is secondarily adsorbed. The hydrogen ions or other ions which are secondarily absorbed, have been termed **counter ions.** Thus the so-called electrical double layer is set up between the particles and the solution. An arsenious sulphide particle is represented diagrammatically in Fig. 1-27. The colloidal particle of arsenious sulphide has a negatively charged surface, with positively charged counter ions which impart a positive charge to the liquid immediately surrounding it. If an electric current is passed through the solution, the negative particles will move towards the anode, although by virtue of the fact that the colloidal particle consists of an aggregate of arsenious sulphide molecules, its mobility will be less than that of ordinary anions.

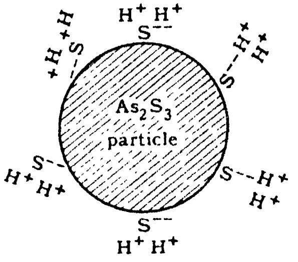

FIG. 1-27.

If the electrical double layer is destroyed, the sol is no longer stable, and the particles will flocculate since the concentration is in excess of the solubility product. Thus if barium chloride solution is added, barium ions are preferentially adsorbed by the particles ; the orientation of the surface is disturbed and the charge disappears. After flocculation, it is found that the dispersion medium is acid owing to the liberation of the hydrogen counter ions. It appears that ions of opposite charge to those primarily adsorbed on the surface are necessary for coagulation. The minimum amount of electrolyte necessary to cause flocculation of the colloid is called the **flocculation** or **coagulation value.** It has been found that the latter depends primarily upon the valency of the ions of the opposite charge to that on the colloidal particles: the nature of the ions has some influence also. This is clearly shown by the results collected in Table XIX.

TABLE XIX. COAGULATION VALUES IN MILLI-MOLS OF COAGULATING ION PER LITRE.

NEGATIVE ARSENIC TRISULPHIDE SOL		POSITIVE HYDRATED FERRIC OXIDE SOL	
Salt	*Coag. Value*	*Salt*	*Coag. Value*
$AlCl_3$	0·062	$K_4Fe(CN)_6$	0·067
$Al_2(SO_4)_3$	0·074	$K_3Fe(CN)_6$	0·096
$FeCl_3$	0·136	K_2SO_4	0·22
$CaCl_2$	0·649	$K_2Cr_2O_7$	0·19
$BaCl_2$	0·691	K_2CrO_4	0·33
$MgCl_2$	0·717	$K_2C_2O_4$	0·24
$Ba(NO_3)_2$	0·687	$KBrO_3$	31
KCl	49·5	KCNS	47
NaCl	51·0	KCl	103
LiCl	58·4	KNO_3	131
KNO_3	50·0	KBr	138
HCl	30·8	KI	154

If two sols of opposite sign are mixed, mutual coagulation usually occurs owing to the neutralisation of charges. The above remarks apply largely to suspensoids. Emulsoids are generally very more difficult to coagulate than suspensoids. If an emulsoid sol, *e.g.*, of gelatin, is added to a suspensoid sol, *e.g.*, of gold, then the suspensoid sol appears to be strongly protected against the flocculating action of electrolytes. It is probable that the particles of the emulsoid sol are adsorbed by the suspensoid and impart their own properties to the latter. The emulsoid is known as a **protective colloid.** This explains the relative stability of the otherwise unstable gold sols produced by the addition of a little gelatin. For this reason also, organic matter, which might form a protective colloid, is generally destroyed before proceeding with an inorganic analysis.

During the flocculation of a colloid by an electrolyte, the ion of opposite sign to that of the colloid is adsorbed to a varying degree on the surface ; the higher the valency of the ion, the more strongly is it adsorbed. In all cases, the precipitate will be contaminated by surface adsorption. Upon washing the precipitate with water, part of the adsorbed electrolyte is removed, and a new difficulty may arise. The electrolyte concentration in the supernatant liquid may fall below the coagulation value, and the precipitate will pass into colloidal solution again. This phenomenon, which is known as **peptisation,** is of great importance in quantitative analysis. By way of illustration, let us consider the precipitation of silver by excess of chloride ions in acid solution and the subsequent washing of the coagulated silver chloride with water ; the adsorbed hydrogen ions will be removed by the washing process and a portion of the precipitate will pass through the filter. If, however, washing is carried out with dilute nitric acid, no peptisation occurs. For this reason, precipitates are always washed with a suitable solution of an electrolyte which does not interfere with the subsequent steps in the estimation.

The adsorptive properties of colloids find a number of applications in analysis, *e.g.*, in the removal of phosphates by hydrated stannic oxide in the presence of nitric acid, in the use of adsorption indicators (Section **I, 42**), in the qualitative detection and colorimetric estimation of elements and radicals with many organic reagents (for example, aluminium with " aluminon " Section **V, 15**).

I, 57. Supersaturation and precipitate formation.—The solubility of a substance at any given temperature in a given solvent is the amount of the substance dissolved by a known weight of that solvent when the substance is in equilibrium with the solvent. The solubility depends upon the particle size, when these are smaller than about 0·01 mm. in diameter ; the solubility increases greatly the smaller the particles owing to the increasing rôle played by surface effects (compare Table XVIII). The definition of solubility given above refers to particles larger than 0·01 mm. A supersaturated solution is one that contains a greater concentration of solute than corresponds to the equilibrium solubility at the temperature under consideration. Supersaturation is therefore an unstable state which may be brought to a state of stable equilibrium by the addition of a crystal of the solute (" seeding " the solution) or of some other substance, or by mechanical means such as shaking or stirring. The difficulty of precipitation of magnesium ammonium phosphate will at once come to mind as an example of supersaturation.

According to von Weimarn (1913, 1925) supersaturation plays an important part in determining the particle size of a precipitate. He has deduced that the initial velocity of precipitation is proportional to $(Q - S)/S$, where Q is the total concentration of the substance that is to precipitate, and S is the equilibrium solubility ; $(Q - S)$ will denote the supersaturation at the moment precipitation commences. The expression applies approximately only when Q is large as compared with S. The influence of the degree of supersaturation is well illustrated by von Weimarn's results for the formation of barium sulphate from solutions of barium thiocyanate and manganese sulphate respectively. These are collected in Table XX below. The results clearly show that the particle size of a precipitate decreases with increasing concentration of the reactants. For the production of a crystalline precipitate, for which the adsorption errors will be least and filtration will be easiest, $(Q - S)/S$ should be as small as possible. There is obviously a practical limit to reducing $(Q - S)/S$ by making Q very small, since for a precipitation to be of value in analysis, it must be complete in a comparatively short time and the volumes of solutions involved must not be too large. There is, however, another method which may be used, *viz.*, that of increasing S. For example, barium sulphate is about fifty times more soluble in $2N$ hydrochloric acid: if $0{\cdot}1N$ solutions of barium chloride

TABLE XX. SEPARATION OF $BaSO_4$ AT VARIOUS DEGREES OF SUPERSATURATION (VON WEIMARN).

Concentration of Reagents	$(Q - S)/S$	*Type of Precipitate*
$7N$	175,000	A gelatinous precipitate is formed, and practically the whole of the water is adsorbed; the containing vessel can be inverted without the contents running out. The gel is unstable, and growth of the large crystals at the expense of small ones is very rapid; after a few hours the precipitate becomes opaque.
$3N$	75,000	Gelatinous films formed; become turbid after one minute.
N	25,000	Primary precipitate is curdy and of colloidal dimensions. Particles appear as points at a magnification of 1500 x.
$0{\cdot}05N$	1300	Primary precipitate consists of feathery and star-shaped crystal skeletons.
$0{\cdot}005N$	125	Precipitate consists of compact crystal skeletons.
ca. $0{\cdot}001N$	25	Solution becomes opalescent during first five minutes, and precipitation continues for 2 to 3 hours. After that time crystals have a length of 0·005 mm.
ca. $0{\cdot}0002N$	5	Precipitate appears after about a month. At the end of six months, the length of the largest crystals is about 0·03 mm. and their breadth 0·015 mm.

and sulphuric acid are prepared in $2N$ boiling hydrochloric acid and the solutions mixed, a typical crystalline precipitate of barium sulphate is slowly formed.

The applications of the above conceptions* are to be found in the following recognised procedures in gravimetric analysis :

1. Precipitation is usually carried out in hot solutions, since the solubility generally increases with temperature.
2. Precipitation is effected in dilute solution and the reagent is added slowly and with thorough stirring. The slow addition results in the first particles precipitated acting as nuclei for the deposition of new particles as they are formed.
3. A suitable reagent is often added to increase the solubility of the precipitate and thus lead to larger primary particles.

I, 58. The purity of the precipitate. Coprecipitation.—When a precipitate separates from a solution, it is not always perfectly pure : it may contain varying amounts of impurities dependent upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed **coprecipitation.** We must distinguish between two important types of coprecipitation. The first is concerned with adsorption at the *surface* of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles.

With regard to surface adsorption, this will, in general, be greatest for gelatinous precipitates and least for those of pronounced macro-crystalline character. Precipitates with ionic lattices appear to conform to the Paneth-Fajans-Hahn adsorption rule, which states that " those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice." Thus silver iodide adsorbs silver acetate much more strongly than silver nitrate under comparable conditions since the former is the less soluble. The deformability of the adsorbed ions and the electrolytic dissociation of the adsorbed compound also have a considerable influence ; the smaller the dissociation of the compound, the greater is the adsorption. Thus hydrogen sulphide, a weak electrolyte, is strongly adsorbed by metallic sulphides.

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* For a detailed discussion, see T. B. Smith, *Analytical Processes,* 1929 (Arnold and Co.).

The second type of coprecipitation may be visualised as occurring during the building up of the precipitate from the primary particles. The latter will be subject to a certain amount of surface adsorption, and during their coalescence the impurities will either be partially eliminated if large single crystals are formed and the process takes place slowly, or, if coalescence is rapid, large crystals composed of loosely bound small crystals may be produced and some of the impurities may be entrained within the walls of the large crystals. If the impurity is isomorphous or forms a solid solution with the precipitate, the amount of coprecipitation may be very large, since there will be no tendency for elimination during the " ageing " process. The latter actually occurs during the precipitation of barium sulphate in the presence of alkali nitrates ; in this particular case X-ray studies have shown that the abnormally large coprecipitation (which may be as high as 3·5 per cent if precipitation occurs in the presence of high concentrations of nitrate) is due to the formation of solid crystals. Fortunately, however, such cases are comparatively rare in analysis.

Appreciable errors may also be introduced by **post-precipitation.** This is the precipitation which occurs on the surface of the first precipitate *after* its formation. It occurs with sparingly soluble substances which form supersaturated solutions ; they usually have an ion in common with the primary precipitate. Thus in the precipitation of calcium as oxalate in the presence of magnesium, magnesium oxalate separates out gradually upon the calcium oxalate ; the longer the precipitate is allowed to stand in contact with the solution, the greater is the error due to this cause. A similar effect is observed in the precipitation of copper or mercuric sulphide in 0·3*N* hydrochloric acid in the presence of zinc ions ; zinc sulphide is slowly post-precipitated.

It is convenient to consider now the influence of **digestion.** This is usually carried out by allowing the precipitate to stand for 12 to 24 hours at room temperature, or sometimes by warming the precipitate for some time, in contact with the liquid from which it was formed : the object is, of course, to obtain complete precipitation in a form which can be readily filtered. During the process of digestion or of the ageing of precipitates, at least two changes occur. The very small particles, which have a greater solubility than the larger ones, will, after precipitation has occurred, tend to pass into solution, and will ultimately redeposit upon the larger particles; the coprecipitation on the minute particles is thus eliminated and the total coprecipitation on the ultimate precipitate reduced. The rapidly formed crystals are probably of irregular shape and possess a comparatively large internal surface; upon digestion these tend to become more regular in character, thus resulting in a decrease in the area of the internal surface and a consequent reduction of adsorption. The net result of digestion is usually to reduce the extent of coprecipitation and to increase the size of the particles, rendering filtration easier.

I, 59. Conditions of precipitation.—No universal rules for precipitation can be given which are applicable to all cases of precipitation, but, with the aid of an intelligent application of the facts enumerated in the foregoing paragraphs, a number of fairly general rules may be stated:

1. Precipitation should be carried out in dilute solution. due regard being paid to the solubility of the precipitate, the time required for filtration and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to coprecipitation.

2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be necessary. In some instances the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation (compare Section **I, 58**).

3. Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other most favourable temperature. At the higher temperature (*a*) the solubility is increased with a consequent reduction in the degree of supersaturation, (*b*) coagulation is assisted and sol formation decreased, and (*c*) the velocity of crystallisation is increased, thus leading to better-formed crystals.

4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of

coprecipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.

5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptisation. (For theory of washing, see Section **I, 60** below.)

6. If the precipitate is still appreciably contaminated as a result of coprecipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then reprecipitating it. The amount of foreign substance present in the second precipitation will be small, and consequently the amount of the entrainment of the precipitate will also be small.

I, 60. Washing of the precipitate.—The experimental aspect of this important subject is dealt with in Section **II, 34.** Only some general theoretical considerations will be given here. Most precipitates are produced in the presence of one or more soluble compounds, and it is the object of the washing process to remove these as completely as possible. It is evident that only surface impurities will be removed in this way. The composition of the wash solution will depend upon the solubility and chemical properties of the precipitate and upon its tendency to undergo peptisation, the impurities to be removed, and the influence of traces of the wash liquid upon the subsequent treatment of the precipitate before weighing. Water cannot, in general, be employed owing to the possibility of producing partial peptisation of the precipitate and, in many cases, the introduction of small losses as a consequence of the slight solubility of the precipitate. A solution of some electrolyte is employed. This should possess a common ion with the precipitate in order to reduce solubility errors, and should easily be volatilised in the preparation of the precipitate for weighing. For these reasons, ammonium salts, ammonia solution and dilute acids are commonly employed. If the filtrate is required in a subsequent determination, the selection is limited to substances which will not interfere in the sequel. Also hydrolysable substances will necessitate the use of solutions containing a salt which will depress the hydrolysis (compare Section **I, 18**). As examples of washing liquids we may mention very dilute nitric acid for the silver halides, and dilute ammonium oxalate solution for calcium oxalate. Whether the wash liquid is employed hot or at some other temperature will depend primarily upon the solubility of the precipitate; if permissible, hot solutions are to be preferred, because of the greater solubility of the foreign substances and the increased speed of filtration.

Solubility losses are reduced by employing the minimum quantity of wash solution consistent with the removal of impurities. It can be readily shown that washing is more efficiently carried out by the use of many small portions of liquid than with a few large portions, the volume being the same in both instances. Under ideal conditions, where the foreign body is simply mechanically associated with the particles of the precipitate, the following expression may be shown to hold*:

$$x_n = x_0 \left(\frac{u}{u + v} \right)^n ,$$

where x_0 is the concentration of impurity before washing, x_n is the concentration of impurity after n washings, u is the volume in ml. of the liquid remaining with the precipitate after draining, and v is the volume in ml. of the solution used in each washing. It follows from this expression that it is best (*a*) to allow the liquid to drain as far as possible in order to maintain u at a minimum, and (*b*) to use a relatively small volume of liquid and to increase the number of washings. Thus if $u = 1$ ml. and $v = 9$ ml., five washings would reduce the surface impurity to 10^{-6} of its original value; one washing with the same volume of liquid, *viz.*, 45 ml., would only reduce the concentration to 1/46 or $2 \cdot 2 \times 10^{-2}$ of its initial concentration.

In practice the washing process is not quite so efficient as the above simple theory would indicate, since the impurities are not merely mechanically associated with the surface. Furthermore, solubility losses are not so great as one would expect from the solubility data because the wash solution passing through the filter is not saturated with respect to the precipitate. Frequent qualitative tests must be made upon portions of the filtrate for some foreign ion which is known to be present in the original solution; as soon as these tests are negative, the washing is discontinued.

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* T. B. Smith, *Analytical Processes*, 1929, p. 48 (Arnold and Co.); see also J. W. Mellor and H. V. Thompson, *A Treatise on Quantitative Inorganic Analysis*, 1938, p. 84 (C. Griffin and Co. Ltd.).

QUANTITATIVE SEPARATIONS BASED UPON PRECIPITATION METHODS

I, 61. Fractional precipitation.—The simple theory of fractional precipitation has been given in Section **I, 11.** It was shown that when the solubility products of two sparingly soluble salts having an ion in common differ sufficiently, then one salt will precipitate almost completely before the other commences to separate. This separation is actually possible for a mixture of chloride and iodide, but in other cases the theoretical predictions must be verified experimentally because of the danger of coprecipitation (Section **I, 58**) affecting the results. Some separations based upon fractional precipitation, which are of practical importance, will now be considered.

(**A**) **Precipitation of sulphides.** In order to fully understand the separations dependent upon the sulphide ion, we shall consider first the quantitative relationships involved in a saturated solution of hydrogen sulphide. The following equilibria are present :

$$H_2S \rightleftharpoons H^+ + HS^- ;$$
$$HS^- \rightleftharpoons H^+ + S^{--}.$$
$$[H^+] \times [HS^-] \,/\, [H_2S] = K_1 = 9{\cdot}1 \times 10^{-8} \qquad \text{(i)}.$$
$$[H^+] \times [S^{--}] \,/\, [HS^-] = K_2 = 1{\cdot}2 \times 10^{-15} \qquad \text{(ii)}.$$

The very small value of K_2 indicates that the secondary dissociation and consequently $[S^{--}]$ is exceedingly small. It follows therefore that only the primary ionisation is of importance, and $[H^+]$ and $[HS^-]$ are practically equal in value. A saturated aqueous solution of hydrogen sulphide at 25°C, at atmospheric pressure, is approximately 0·1 molar. Substituting $[H^+] = [HS^-]$ and $[H_2S] = 0{\cdot}1$ in equation (i), we obtain :

$$[H^+] = [HS^-] = \sqrt{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1} = 9{\cdot}5 \times 10^{-5}.$$

Both the equilibrium equations must be satisfied simultaneously ; by substitution of these values for $[H^+]$ and $[HS^-]$ in equation (ii), we obtain :

$$9{\cdot}5 \times 10^{-5} \times [S^{--}] = 1{\cdot}2 \times 10^{-15} \times 9{\cdot}5 \times 10^{-5},$$
$$\text{or } [S^{--}] = 1{\cdot}2 \times 10^{-15},$$

which is the value for K_2.

If we multiply equations (i) and (ii) together, we obtain :

$$\frac{[H^+]^2 . [S^{--}]}{[H_2S]} = 1{\cdot}1 \times 10^{-22} \qquad \text{(iii)},$$

or

$$[S^{--}] = 1{\cdot}1 \times 10^{-23} \,/\, [H^+]^2 \qquad \text{(iii')}.$$

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen ion concentration. By varying the *p*H of the solution, the $[S^{--}]$ may be controlled; in this way separations of metallic sulphides may be effected. Let us first calculate the $[S^{--}]$ in a solution of 0·25 molar hydrochloric acid saturated with hydrogen sulphide ; this is the concentration employed for the precipitation of the sulphides of the Group II metals in qualitative analysis. The total concentration of H_2S will be approximately the same as in aqueous solution, *i.e.*, 0·1*M* : the $[H^+]$ will be equal to that of the completely dissociated hydrochloric acid, *i.e.*, 0·25*M*, but the $[S^{--}]$ will be reduced below $1{\cdot}2 \times 10^{-15}$. Substituting in equations (i) and (ii) :

$$[HS^-] = \frac{9{\cdot}1 \times 10^{-8} \times [H_2S]}{[H^+]} = \frac{9{\cdot}1 \times 10^{-8} \times 0{\cdot}1}{0{\cdot}25} = 3{\cdot}6 \times 10^{-8},$$

$$[S^{--}] = \frac{1{\cdot}2 \times 10^{-15} \times [HS^-]}{[H^+]} = \frac{1{\cdot}2 \times 10^{-15} \times 3{\cdot}6 \times 10^{-8}}{0{\cdot}25} = 1{\cdot}7 \times 10^{-22}.$$

Thus by changing the acidity from $9{\cdot}5 \times 10^{-5}M$ (that present in saturated hydrogen sulphide water) to 0·25*M*, the sulphide ion concentration is reduced from $1{\cdot}2 \times 10^{-15}$ to $1{\cdot}7 \times 10^{-22}$.

With the aid of a table of solubility products of metallic sulphides (see Section **I, 8,** Table IV), we can calculate whether certain sulphides will precipitate under any given conditions of acidity and also the concentration of the metallic ions remaining in solution. Precipitation of a metallic sulphide MS will occur when $[M^{++}] \times [S^{--}]$ exceeds the solubility product, and the concentration of metallic ions remaining in the solution may be calculated from the equation :

$$[M^{++}] = \frac{S_{MS}}{[S^{--}]} = \frac{S_{MS} \times [H^+]^2}{1{\cdot}1 \times 10^{-22} \times [H_2S]} \qquad \text{(iv)},$$

As an example we may consider the precipitation of cupric sulphide ($S_{CuS} = 8{\cdot}5 \times 10^{-45}$) and ferrous sulphide ($S_{FeS} = 1{\cdot}5 \times 10^{-19}$) from 0·01*M* solutions of the metallic ions in the presence of 0·25*M* hydrochloric acid. For cupric sulphide, the solubility product is readily exceeded $[S^{--}] = 1{\cdot}7 \times 10^{-22}$, $[Cu^{++}] = 0{\cdot}01$ and precipitation will occur until

$$[Cu^{++}] = 8{\cdot}5 \times 10^{-45} \times (H^+]^2 \,/\, 1{\cdot}1 \times 10^{-22} \times [H_2S],$$
$$= 8{\cdot}5 \times 10^{-45} \times (0{\cdot}25)^2 \,/\, 1{\cdot}1 \times 10^{-22} \times 0{\cdot}1,$$
$$= 5 \times 10^{-23},$$

i.e., precipitation is virtually complete. With ferrous sulphide, the solubility product cannot be exceeded and precipitation will not occur under these conditions. If, however, the acidity is sufficiently decreased, and consequently $[S^{--}]$ increased, ferrous sulphide will be precipitated.

The case of zinc sulphide is of especial interest. Various values are given in the literature for its solubility product: the most trustworthy figures vary between 1×10^{-24} and 8×10^{-26}. If we accept the latter figure, then we should expect precipitation to occur in a, say, 0·01*M* solution of zinc ions in the presence of 0·25*M* hydrochloric acid, since the S.P. should be exceeded; furthermore, the residual zinc ion concentration should be $4{\cdot}7 \times 10^{-4}$ when computed as described above. In practice, precipitation does not occur at this acidity. This may be partly due to the great tendency that zinc sulphide possesses to remain in supersaturated solution, but is perhaps best explained as follows. The above figure for the solubility product refers to a solution in equilibrium with relatively large particles, whereas for precipitation to occur it is necessary that the S.P. of the particles *actually formed* should be exceeded. It may well be that under the above experimental conditions these are extremely small, thus possessing a greater solubility (Section **I, 56**) and a greater solubility product; precipitation will therefore not take place. This view is supported by the fact that post-precipitation of zinc sulphide (compare Section **I, 58**) will occur upon the surface of other metallic sulphides, such as those of copper and mercury. It is possible to precipitate zinc in acid solution provided the experimental conditions are very carefully controlled, e.g., when the *p*H of the solution lies between 2 and 3 and ammonium salts are present as coagulants: this is attained by the use of a buffer mixture of formic acid and ammonium formate, and ammonium sulphate or of chloroacetic acid and sodium acetate. It is probable that large particles of zinc sulphide are initially formed under these conditions.

(B) Precipitation and separation of hydroxides at controlled hydrogen ion concentration or *p*H. The underlying theory is very similar to that just given for sulphides. Precipitation will depend largely upon the solubility product of the metallic hydroxides and the hydroxyl ion concentration (or upon the hydrogen ion concentration, since $p\text{H} + p\text{OH} = pK_w$—Section **I, 17**) of the solution.

We have seen that the sulphide ion concentration of a saturated aqueous solution of hydrogen sulphide may be controlled within wide limits by suitably changing the concentration of hydrogen ions—a common ion—of the solution. In a like manner the hydroxyl ion concentration of a solution of a weak electrolyte, such as ammonium hydroxide ($K_b = 1{\cdot}8 \times 10^{-5}$), may be regulated by the addition of a common ion, *e.g.*, ammonium ions in the form of the completely dissociated ammonium chloride. The magnitude of the effect is best illustrated by means of an example. In a 0·1 molar ammonia solution, the degree of dissociation is given (Section **I, 4**) approximately by :

$$a = \sqrt{Kc} = \sqrt{1{\cdot}8 \times 10^{-5} \times 0{\cdot}1} = 0{\cdot}013.$$

Hence $[\text{OH}^-] = 0{\cdot}0013$, $[\text{NH}_4^+] = 0{\cdot}0013$, and $[\text{NH}_4\text{OH}] = 0{\cdot}0987$. Let us calculate the change in the degree of dissociation and of $[\text{OH}^-]$ upon the addition of 0·5 gram molecule (26·75 g.) of ammonium chloride to one litre of the 0·1 molar ammonia solution. If a' is the degree of dissociation in the presence of the added ammonium chloride, then :

$$[\text{OH}^-] = a'c = 0{\cdot}1a', \text{ and } [\text{NH}_4\text{OH}] = (1 - a')c = 0{\cdot}1,$$

since a' may be taken as negligibly small. The addition of the completely dissociated ammonium chloride will of necessity decrease the $[\text{NH}_4^+]$ derived from the base and increase $[\text{NH}_4\text{OH}]$ since K_b is constant under all conditions. Now, as a first approximation, $[\text{NH}_4^+] = 0{\cdot}5$.

Substituting this value in the equation :

$$\frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{0{\cdot}5 \times 0{\cdot}1a'}{0{\cdot}1} = 1{\cdot}8 \times 10^{-5},$$

$$a' = 3{\cdot}6 \times 10^{-5} \text{ and } [\text{OH}^-] = 3{\cdot}6 \times 10^{-6}.$$

Thus the addition of half an equivalent weight of ammonium chloride to a 0·1 molar solution of ammonium hydroxide has decreased the hydroxyl ion concentration from 0·0013 to 0·0000036, or has changed *p*OH from 2·9 to 5·4, *i.e.*, the *p*H has changed from 11·1 to 8·6.

An immediate application of the use of the ammonium hydroxide-ammonium chloride mixture may be made to the familiar example of the prevention of precipitation of magnesium hydroxide (S.P. $1{\cdot}5 \times 10^{-11}$). We can first compute the minimum hydroxyl ion concentration necessary to prevent precipitation in, say, 0·1 molar magnesium solution.

$$[\text{OH}^-] = \sqrt{\frac{S_{\text{Mg(OH)}_2}}{[\text{Mg}^{++}]}} = \sqrt{\frac{1{\cdot}5 \times 10^{-11}}{0{\cdot}1}} = 1{\cdot}22 \times 10^{-5}M.$$

or $p\text{OH} = 4{\cdot}9$ and $p\text{H} = 14{\cdot}0 - 4{\cdot}9 = 9{\cdot}1$.

If we employ an ammonium hydroxide solution which is 0·1 molar, the concentration of $[\text{NH}_4^+]$ ion as ammonium chloride or other ammonium salt necessary to prevent the precipitation of magnesium hydroxide can be readily calculated as follows. Substituting in the mass action equation :

$$\frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1{\cdot}8 \times 10^{-5},$$

$$\frac{[\text{NH}_4^+] \times 1{\cdot}22 \times 10^{-5}}{0{\cdot}1} = 1{\cdot}8 \times 10^{-5},$$

or $$[\text{NH}_4^+] = \mathit{1{\cdot}48} \times \mathit{10^{-1}}M.$$

This corresponds to an ammonium chloride concentration of $1{\cdot}48 \times 10^{-1} \times 53{\cdot}5 = 8{\cdot}2$ g. per litre.

We will now consider the conditions necessary for the practically complete precipitation of magnesium hydroxide from a $0{\cdot}1M$ solution of, say, magnesium chloride. A pOH slightly in excess of 4·9 (*i.e.*, $p\text{H} = 9{\cdot}1$) might fail to precipitate the hydroxide owing to supersaturation. Let us suppose the hydroxyl ion concentration is increased ten times, *i.e.*, to pOH 3·9 or pH 10·1, then, provided no supersaturation is present :

$$[\text{Mg}^{++}] = \frac{S_{\text{Mg(OH)}_2}}{[\text{OH}^-]^2} = \frac{1{\cdot}5 \times 10^{-11}}{(1{\cdot}22 \times 10^{-4})^2} = 0{\cdot}001M,$$

i.e., the concentration of the magnesium ions remaining in solution is $0{\cdot}001M$, or one per cent of the magnesium ions would remain unprecipitated. If pOH is changed to 2·9 or pH to 11·1, it can be shown in a similar way that the concentration of the magnesium ions left in solution is *ca.* $1 \times 10^{-5}M$, so that the precipitation error is 0·1 per cent, a negligible quantity. We may therefore say that magnesium is precipitated quantitatively at a pH of 11·1.

Our knowledge of the solubility products of metallic hydroxides is, however, not very precise, so that it is not always possible to make exact theoretical calculations. The *p*H values at which various hydroxides begin to precipitate from dilute solution are collected in the following table, which is based upon the work of H. T. S. Britton (1925).

*p*H VALUES AT WHICH VARIOUS HYDROXIDES ARE PRECIPITATED.

*p*H	*Metal Ion*	*p*H	*Metal Ion*
3	Sn^{++}, Fe^{+++}, Zr^{++++}	7	Fe^{++}
4	Th^{++++}	8	Co^{++}, Ni^{++}, Cd^{++}
5	Al^{+++}	9	Ag^{+}, Mn^{++}, Hg^{++}.
6	Zn^{++}, Cu^{++}, Cr^{+++}	11	Mg^{++}

One of the easiest, and also a widely employed, separation is that of ferric iron from magnesium. This can be readily effected, as we have just seen, by the use of ammonium chloride-ammonium hydroxide buffer mixture. By proper adjustment of the *p*H of the solution it is possible to separate ferric iron and aluminium from zinc, manganese, nickel, cobalt, and the alkaline earths. This regulation of *p*H is achieved by the addition of the appropriate buffer mixture. It is evident from the above Table that some separations will be much more difficult than others: thus the separation of aluminium and chromium is an example of a difficult separation. The use of ammonia solution is not always satisfactory as it tends to produce, particularly in the case of the trivalent metals, gelatinous precipitates, which are difficult to filter and wash, and also have a marked tendency to adsorb other cations present in solution. For this reason other reagents are employed for the separation of trivalent ions from divalent ions: a few examples will be mentioned below. Reference must, however, be made to the use of the organic bases, such as phenyl-hydrazine, aniline, pyridine, quinoline, etc. Thus phenyl-hydrazine is particularly valuable for separating aluminium from ferrous iron; only the former is precipitated as the hydroxide. The other organic bases are useful in the separation of the rare earths.

In the **basic acetate method** a buffer solution consisting of acetic acid with sodium or ammonium acetate is employed. The acetates of such weak bases as ferric iron are hydrolysed in hot solution and are completely precipitated as basic acetates; the acetates of the strong bases of the divalent metals are much less hydrolysed and, if the *p*H is adequately controlled, are not precipitated. The method is quite satisfactory for the separation of ferric iron from divalent metals such as zinc, manganese, cobalt, nickel, and copper; it is fairly satisfactory for mixtures of iron and aluminium, but not so suitable for aluminium alone; it is inapplicable for chromium.

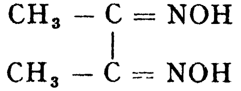
$$Fe(C_2H_3O_2)_3 + 2H_2O \rightleftharpoons 2H.C_2H_3O_2 + Fe(OH)_2.C_2H_3O_2.$$

A modification, introduced by Kolthoff (1934), is to use a benzoic acid—ammonium benzoate buffer mixture, when a good separation of ferric iron, aluminium and chromium from the divalent metals is claimed.

Suspensions of carbonates (*e.g.*, of barium, lead, and cadmium) and of oxides (*e.g.*, of zinc, magnesium and mercury) have been used for the same purpose, since they may be regarded as exerting a buffer action. Their applications are, however, limited; mention may be made of the use of barium or cadmium carbonates for the separation of the trivalent metals of Group IIIA from the divalent metals of Group IIIB.

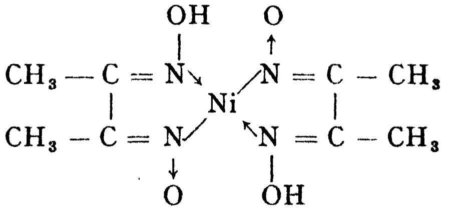
I, 62. Organic precipitants.—A number of organic compounds are available which combine with inorganic ions or compounds to form sparingly soluble and often coloured compounds. With cations, the metal is held either by primary valencies or by co-ordinate links, or by both. These compounds usually have high molecular weights so that a small amount of the ions will yield a relatively large amount of the precipitate. The ideal organic precipitant should be *specific* in character, i.e., it should give a precipitate with only one particular ion. In few cases, however, has this ideal been attained; it is more usual to find that the organic reagent will react with a group of ions, but frequently by a rigorous control of the experimental conditions it is possible to precipitate only one of the ions of the group. Sometimes the precipitated organic compound may be weighed after drying at a suitable temperature; in other cases the composition is not quite definite and the substance is converted by ignition to the oxide of the metal; in a few instances, a volumetric method is employed which utilises the quantitatively precipitated organic complex. Examples of each of these will be given below.

A. Dimethylglyoxime. This reagent (I) was discovered by L. Tschugaeff in 1905



$$\begin{array}{l} CH_3 - C = NOH \\ \quad\quad\;\; | \\ CH_3 - C = NOH \end{array}$$

(I)

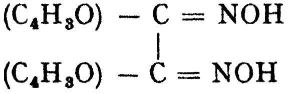


(II)

and was applied by O. Brunck in 1907 for the determination of nickel in steel. It gives a bright red precipitate II or $Ni(C_4H_7O_2N_2)_2$ with nickel salt solutions; precipitation is usually carried out in ammoniacal solution or in a buffer solution containing ammonium acetate and acetic acid. The complex is weighed after drying at 110–120° C. Palladium solutions also give a characteristic precipitate of the composition $Pd(C_4H_7O_2N_2)_2$; this precipitation is carried out in cold solutions containing 2 to 5 per cent by volume of hydrochloric acid. If iron and/or aluminium are present, citric or tartaric acid must be added in order to prevent hydrolysis.

The reagent itself is insoluble in water, and is employed as an approximately 1 per cent solution in alcohol.

α-Furildioxime (III) has also been proposed for the determination of nickel; it gives a red precipitate with nickel salts in slightly ammoniacal solution. Its advantages over dimethylglyoxime are its greater solubility in water, its higher sensitivity (about 7 times greater) and the small nickel content of the complex compound, thus giving a larger weight of precipitate for a given weight of nickel. It is, however, expensive.



$$\begin{array}{l} (C_4H_3O) - C = NOH \\ \quad\quad\quad\quad\;\; | \\ (C_4H_3O) - C = NOH \end{array}$$

(III)

α-Benzildioxime $\{C_6H_5.C(=NOH).C(=NOH).C_6H_5\}$, m.p. 237°C, is a more sensitive reagent for nickel than is dimethylglyoxime, but has the disadvantage that it is less soluble than the latter. It is therefore not usually employed except for the determination of small quantities of nickel. Owing to the voluminous character of the precipitate $Ni(C_{14}H_{11}O_2N_2)_2$

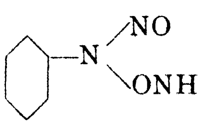
not more than about 0·02 g. of Ni can be accurately determined.

The reagent is prepared by dissolving 0·2 g. of the dioxime in a mixture of 950 ml. of alcohol and 50 ml. of concentrated ammonia solution.

For the **determination of nickel** a slight excess of a warm solution of the reagent is added to the ammoniacal solution of the nickel salt and the whole heated on a water bath to coagulate the precipitate (*ca.* 2 minutes). The precipitate is filtered on a weighed Gooch, sintered glass or porous porcelain crucible, washed with 50 per cent alcohol, followed by hot water, dried to constant weight at 110°C, and weighed as $Ni(C_{14}H_{11}O_2N_2)_2$.

Nitrates and copper must be absent. The interference of ferrous iron and chromium is prevented by the addition of sodium citrate or tartrate ; of zinc and magnesium by ammonium chloride ; of manganese by a slight excess of acetic acid or citric acid and hydrazine (the latter to prevent oxidation of the manganese) ; of cobalt by the addition of excess of the reagent.

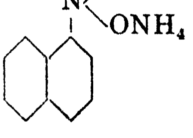
✓ **B. Cupferron (the ammonium salt of nitrosophenylhydroxylamine).**



(IV)

This substance (IV) was introduced by O. Baudisch in 1909 for the separation of copper from iron. It gives sparingly soluble compounds with a number of elements in which the ammonium radical is replaced by one equivalent of the metal in question. Precipitation is made in the cold using a slight excess of a filtered 6 per cent aqueous solution of the reagent. The precipitate cannot be satisfactorily dried, and is therefore converted by ignition into the oxide of the precipitated element and weighed as such. Precipitations are carried out in strongly acid solutions (10 per cent by volume of sulphuric acid or hydrochloric acid), and provide complete separations of elements such as iron, vanadium, titanium, tantalum and zirconium from aluminium, beryllium, chromium, manganese, nickel, zinc and hexavalent uranium. Its principal applications in quantitative analysis are to the determination of iron, titanium, and zirconium.

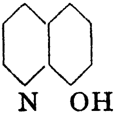
A companion reagent to cupferron, α-**nitroso-naphthylhydroxylamine** or **neo-cupferron** (IVA), was introduced by O. Baudisch in 1937. Its properties are similar to those of cupferron, but the stability of its aqueous solution is not quite so high. Unlike cupferron, however, it may be employed for the quantitative precipitation of small quantities of iron (and of copper)



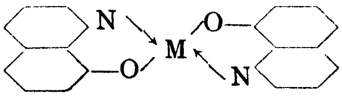
(IVA)

in the presence of aluminium in strong mineral acid media ; it is thus useful for the direct determination of iron in mineral waters and sea waters.*

V. 8-Hydroxyquinoline (oxine). This substance (V) was introduced into quantitative analysis by R. Berg in 1927. It forms sparingly soluble derivatives with metallic ions, which have the composition $M(C_9H_6ON)_2$ (or VI) if the co-ordination number of the metal is four (*e.g.*, magnesium) and $M(C_9H_6ON)_3$ if the co-ordination number is six (*e.g.*, aluminium). There are, however, some exceptions, *e.g.*, $TiO(C_9H_6ON)_2$, $WO_2(C_9H_6ON)_2$ and $MoO_2(C_9H_6ON)_2$. By suitable adjustment of the *p*H of the solution and by other methods (such as the use of organic acids), numerous separations may be carried out, for example, aluminium from beryllium in an ammonium acetate-acetic buffer, magnesium from the alkaline earth metals in ammoniacal solution, and the precipitation of such metals as copper, cadmium, bismuth and zinc under certain experimental conditions.



(V)



(VI)

The complexes are compact and very easy to filter. They may be weighed as such after drying at 100° to 105°C (hydrated " oxinate ") or at 130° to 140°C (anhydrous " oxinate "), or they may be *cautiously* ignited under a cover of oxalic acid and weighed as oxide, or they may be dissolved in hydrochloric acid and titrated with a standard solution of potassium bromate (Section **III, 138**).

The reagent is prepared for use in either of the following ways :—(i) Two grams of oxine are dissolved in 100 ml. of *2N* acetic acid, and ammonia solution is added dropwise until a slight precipitate is just produced : the precipitate is dissolved either by the addition of a little dilute acetic acid or by warming. This solution is stable more or less indefinitely.

(ii) Two grams of oxine are dissolved in 100 ml. of ethyl alcohol, methyl alcohol or acetone. This solution is stable for about 10 days if not exposed to the light.

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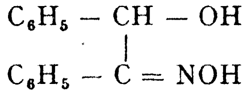
* For further details, see the booklet *Cupferron and Neo-cupferron* (1938) issued by the C. F. Smith Chemical Co., of 867 McKinley Avenue, Columbus, Ohio, U.S.A. This firm supplies a particularly good quality of both cupferron and neo-cupferron. The British agents are F. W. Berk and Co. Ltd., of 52–54 Leadenhall Street, London, E.C.3.

Notes on precipitations with oxine. Precipitation is effected under a variety of conditions, *e.g.*, in acetic acid or alkaline solution by an alcoholic or acetic acid solution of oxine (see above). The reagent is added in excess as indicated by the production of a yellow or orange-yellow colouration in acetic acid or alkaline media respectively. After heating for 2 to 3 minutes, the precipitate is filtered through a filter paper, or a sintered glass (G3 or G4), porous porcelain or Gooch crucible. The filtrate must be yellow or orange-yellow in colour, thus proving the presence of excess of oxine. Frequently the precipitate is washed with hot water until the filtrate is colourless and then with cold water. When too large an excess of oxine is employed for precipitation, the filtrate may become cloudy. This is usually due to oxine which is very much less soluble in cold than in hot water, as is shown by heating the filtrate to the boiling point when the solution becomes clear; a metallic " oxinate " would not pass into solution on boiling.

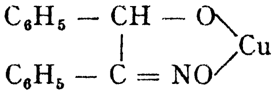
The excess of the reagent from the filtrate and washings may be removed by ether extraction in alkaline solution (pH 8 to 8·5) or, better, by evaporation of the ammoniacal solution with repeated addition of ammonia solution (the oxine is steam-volatile in a slightly alkaline solution). Determinations of other elements by other methods can then be carried out and the concentrated acid or ignition treatment, which is usual with many organic reagents (compare dimethylglyoxime, Section **IV, 89, g** and **f**), is avoided.

D. α-Benzoinoxime (cupron). This reagent (VII) is principally applied in the determination of copper, with which it yields a green precipitate (VIII) in faintly ammoniacal solution; the precipitate is dried at 105–115°C. Ions which are precipitated by ammonia solution are kept in solution by the addition of sodium potassium tartrate. Another important application is to the determination of sexivalent molybdenum which is carried out in fairly strong acid solution; the precipitated compound $Mo_2(C_{14}H_{11}O_2N)_3$ is best ignited at 500–525°C and weighed as MoO_3.

(VII)



$$\begin{array}{l} C_6H_5 - CH - OH \\ \qquad\quad | \\ C_6H_5 - C = NOH \end{array}$$

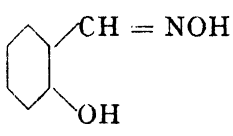


$$\begin{array}{l} C_6H_5 - CH - O \diagdown \\ \qquad\quad | \qquad\qquad Cu \\ C_6H_5 - C = NO \diagup \end{array}$$

(VIII)

The reagent is employed as a 2 per cent solution in rectified spirit.

E. Salicylaldoxime. This substance (IX) is a specific reagent for copper if precipitation is carried out in the presence of acetic acid (compare, however, Section **IV, 32B**). The greenish yellow precipitate $Cu(C_7H_6O_2N)_2$ is weighed after drying at 100–105°C.



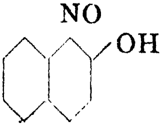
(IX)

The reagent is prepared by dissolving 1 g. of salicylaldoxime in 4–5 ml. of cold 95 per cent alcohol and pouring the solution into 95 ml. of water at a temperature not exceeding 80°C; the mixture is shaken until clear and filtered, if necessary.

Another, and less expensive, method is to add 2·22 g. of pure salicylaldehyde dissolved in 8 ml. of 95 per cent alcohol to 1·27 g. of A.R. hydroxylamine hydrochloride dissolved in 2 ml. of water. The resultant solution is diluted with 15 ml. of 95 per cent alcohol and stirred into 225 ml. of water at 80°C. When cold, the solution is filtered, if necessary. This is an approximately 1 per cent solution of salicylaldoxime.

Salicylaldoxime decomposes slowly in solution; the reagent cannot be kept for more than about 3 days.

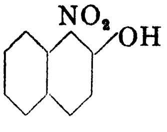
F. α-Nitroso-β-naphthol. This compound (X) reacts with a number of elements to form insoluble compounds in which the hydroxyl hydrogen is replaced by an equivalent of the metal in question. It was first recommended for the separation of cobalt from nickel by Ilinski and V. Knorre in 1885. Precipitations are usually effected by adding the cold reagent to a very dilute hydrochloric acid solution of the metal, and heating to 60–70°C. The following elements are quantitatively precipitated: iron, cobalt, palladium, silver and gold; tin, titanium, vanadium, chromium, copper, molybdenum and tungsten are partially precipitated. Separation is thus effected from aluminium, manganese, nickel, zinc, magnesium, and the alkaline earth metals. The reagent is therefore far from being specific, and preliminary separations are necessary. Its principal use is for the determination of cobalt in the presence of nickel; the red precipitate, $Co(C_{10}H_6O_2N)_3$, obtained by precipitation of cobaltous solutions, is contaminated with a little of a cobaltous salts and some of the reagent, so that it cannot be weighed as such; moreover, ignition in air does not give a perfectly pure cobalt oxide, Co_3O_4. However, if the cobaltous salt is first converted into cobaltic hydroxide $Co(OH)_3$ by means of 100-volume hydrogen peroxide and sodium hydroxide solution, the precipitate dissolved in acetic acid and then precipitated with the reagent, then pure $Co(C_{10}H_6O_2N)_3,2H_2O$ is precipitated, which may be weighed after drying at 130°C. Palladium may be similarly precipitated and weighed as $Pd(C_{10}H_6O_2N)_2$, after drying at 135°C; this method may be used for separation from platinum.



(X)

The reagent is prepared by dissolving 4 grams of α-nitroso-β-naphthol in 100 ml. of glacial acetic acid and then adding 100 ml. of hot distilled water. The filtered solution must be used immediately. The solution is comparatively unstable and should be prepared as required.

G. α-Nitro-β-Naphthol. This compound (XI) acts similarly as a precipitant to α-nitroso-β-naphthol (*e.g.*, it can be used for the determination of cobalt in the presence of nickel, zinc, manganese, aluminium, chromium, and iron, and also for the determination of palladium in the presence of platinum), but it has the great advantage that its aqueous solution is stable. It should therefore be employed in preference to the nitroso compound. Cobalt is precipitated (hydrogen peroxide and sodium hydroxide method) as $Co(C_{10}H_6O_3N)_3$ and may be weighed as such after drying at 130°C. Palladium is precipitated as $Pd(C_{10}H_6O_3N)_2$ and may be weighed in this form after drying at 130°–135°C.



(XI)

Preparation of α-nitro-β-naphthol from α-nitroso-β-naphthol. Stir α-nitroso-β-naphthol with 10 times its weight of water and add slowly an equal volume of nitric acid (*d* 1·25). After a short time, the yellow needles of the nitroso compound conglomerate into flocks and the odour of nitrous acid becomes apparent. The reaction is complete after one hour. Wash the yellowish-grey precipitate thoroughly with water, then heat it with 30 parts of 1 per cent sodium hydroxide solution, and filter. Acidify the clear solution with acetic acid and filter off the yellow precipitate of α-nitro-β-naphthol. Wash with water and recrystallise from hot alcohol. The pure compound has m.p. 103°C.

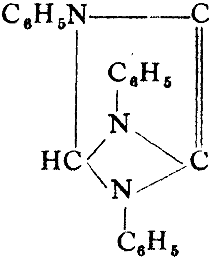
The reagent is prepared by dissolving 2 g. of α-nitro-β-naphthol in 100 ml. of cold glacial acetic acid, diluting with 100 ml. of hot water, and filtering.

H. Phenylthiohydantoic acid
($C_6H_5 - NH - C(=NH) - S - CH_2 - COOH$). Certain elements in ammoniacal or preferably in ammonium citrate containing solution react with phenylthiohydantoic acid ; an equivalent of the element replaces the carboxyl hydrogen. Separation of cobalt and of copper and other elements of Group II from aluminium, chromium, titanium, vanadium, uranium, tungsten, molybdenum, zinc, manganese, calcium and magnesium can thus be effected in one operation. Nickel is partially precipitated, but the product is soluble in concentrated ammonia solution. The precipitate with cobalt is

not of definite composition ; it may be ignited to Co_3O_4. The latter, however, is not quite pure ; it may be fused with potassium pyrosulphate, the cool melt dissolved in water, and cobalt estimated by some other method (see Section **IV, 33**).

The reagent is employed in the form of a 3 per cent aqueous or alcoholic solution.

I. Nitron (1:4 - diphenyl-3 : 5-endanilo - 4 : 5-dihydro-1 : 2 : 4-triazole). Nitron (XII) is a strong base; it precipitates nitrates as the sparingly soluble crystalline nitrate $C_{20}H_{16}N_4,HNO_3$ from solutions slightly acified with sulphuric acid. The solubility of nitron nitrate in very dilute sulphuric acid at 20°C is 10 mg. of salt per 100 ml. of saturated solution, which is equivalent to 1·7 mg. of HNO_3. The following acids form slightly soluble salts with nitron and therefore interfere with the determination : perchloric, thiocyanic, hydriodic, hydrobromic, hydrochloric, chromic, chloric, and nitrous acids.



(XII)

The reagent is employed as a 10 per cent solution in 5 per cent acetic acid.

J. Tannin. Common tannin or tannic acid is essentially a colloidal suspension of negatively charged particles capable of flocculating the positively charged particles of certain inorganic compounds, such as the sols of metallic hydroxides. The separation of various elements depends to a large extent upon the proper adjustment of the *p*H of the solution.

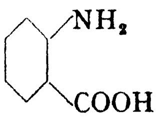
This reagent in the form of a freshly-prepared 3 per cent or 10 per cent aqueous solution is useful for the separation of some of the so-called rarer elements. It may be employed *inter alia* for the quantitative determination of titanium and tungstates, for the separation of aluminium, chromium, iron, etc., from beryllium, and of niobium from tantalum. In most cases the element is ultimately ignited and weighed as the oxide.

K. Phenylarsonic acid. ($C_6H_5.AsO(OH)_2$). This reagent is particularly useful for the determination of tin ; zirconium and thorium are the only elements commonly associated with tin which interfere. The complex is ignited to and weighed as stannic oxide.

The reagent consists of a saturated aqueous solution of phenylarsonic acid (an approximately 10 per cent solution).

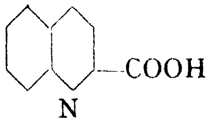
L. Pyridine. Pyridine forms insoluble complexes with the thiocyanates of cadmium, copper, nickel, cobalt, zinc and manganese ; these have the general formula $Me(CNS)_2,(C_5H_5N)_n$ ($n = 4$ for Co, Ni and Mn ; $n = 2$ for Cu, Cd and Zn) (G. Spacu and co-workers, 1927→). In practice, alkali thiocyanate and a few ml. of pure pyridine are added to the neutral or very faintly acid solution of the metal ions. The complexes are readily filtered. They are washed first with water, then with dilute alcohol (both containing a little alkali thiocyanate and pyridine), followed successively by absolute alcohol and absolute ether, each containing a little pyridine. The precipitates are weighed after drying in a vacuum desiccator for 5 to 30 minutes at the laboratory temperature. The method is rapid, but, as is evident, many ions interfere. The results for manganese are not satisfactory because of the slight solubility of the complex in the wash solutions. The method is applicable in the presence of alkali and alkaline earth metals and of magnesium ; considerable quantities of ammonium salts must be absent.

M. Anthranilic acid. This substance (XIII) is employed in the form of a 3 per cent solution of its sodium salt. It gives precipitates with neutral or weakly acetic acid solutions of zinc, cobalt, nickel, cadmium, copper, lead and mercuric mercury ; these have the general formula $Me(C_7H_6O_2N)_2$ (H. Funk and co-workers, 1933-34). The precipitates are crystalline, insoluble in water and alcohol, and non-hygroscopic ; they may be dried at 105°-110°C. The reagent has been employed for the determination of zinc, nickel, cobalt, cadmium, and copper, but offers no great advantages over other reagents for these ions. Its use will therefore not be described in Chapter IV. It may, however, be pointed out that it is essential to employ pure anthranilic acid, m.p. 145°C, in the preparation of the reagent.



(XIII)

N. Quinaldinic acid. This substance (XIV) gives insoluble complexes with the ions of copper, lead, silver, cadmium, zinc, manganese, nickel, cobalt, and ferrous iron, and insoluble basic salts with ferric iron, uranium (uranyl), aluminium, chromium, beryllium, and titanium. In sulphuric acid solution, however, and in the absence of iron and zinc, quinaldinic acid is a specific reagent for copper; the precipitate has the formula $Cu(C_{10}H_6O_2N)_2, H_2O$ and may be weighed in this form after drying at 125°C. The reagent is useful for the rapid estimation of zinc (as $Zn(C_{10}H_6O_2N)_2,H_2O$) and of cadmium (as $Cd(C_{10}H_6O_2N)_2$) in the absence of interfering elements; in both cases the precipitate is dried at 125°C.

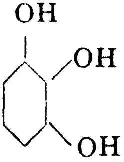


(XIV)

The reagent is prepared by dissolving 2·50 g. of quinaldinic acid or 2·82 g. of the sodium salt in 75 ml. of water.

Note on the recovery of quinaldinic acid. The reagent is expensive, but may be recovered after use. The precipitate and filtrate are best treated separately. The filtrate from a determination is acidified with dilute sulphuric acid and precipitated as copper quinaldinate with copper sulphate solution; the precipitate is filtered, washed, suspended in water, decomposed with hydrogen sulphide, filtered from cupric sulphide, the filtrate evaporated to dryness, and the residue recrystallised from glacial acetic acid. The pure acid has m.p. 155°–156°C. The copper and cadmium complexes are decomposed with hydrogen sulphide and treated as above. Zinc quinaldinate is best dissolved in dilute hydrochloric acid or dilute sulphuric acid, the solution diluted until a precipitate just appears, and then precipitated with copper sulphate solution, etc.

O. Pyrogallol. This compound (XV) yield insolubles complex salts with antimony and bismuth, and may be employed for the quantitative determination of these elements either alone or in the presence of arsenic, lead, etc.



(XV)

The reagent consists of a solution in air-free water. The pyrogallol should have the correct m.p. (133°C), and should leave no residue when heated upon platinum or silica.

P. Ethylenediamine ($NH_2.CH_2.CH_2.NH_2$). Ethylenediamine yields a complex cation with cupric ions:

$$Cu^{++} + 2NH_2.CH_2.CH_2.NH_2 = [Cu(NH_2.CH_2.CH_2.NH_2)_2]^{++} \equiv [Cu\ en_2]^{++} .$$

This reacts with the complex ions $[HgI_4]^{--}$ or $[CdI_4]^{--}$ to yield the insoluble complex salts $[Cu\ en_2][HgI_4]$ and $[Cu\ en_2][CdI_4]$ respectively :

$$HgCl_2 + 4KI = K_2[HgI_4] + 2KCl ;$$

$$K_2[HgI_4] + [Cu\ en_2](NO_3)_2 = [Cu\ en_2][HgI_4] + 2KNO_3.$$

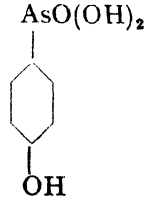
The complex salts are insoluble in water, 95 per cent alcohol and ether, and hence may be employed in the rapid determination of mercury, cadmium and copper respectively (G. Spacu and co-workers, 1929 →). The mercury complex is stable in air and in a vacuum, and its precipitation is unaffected by the presence of ammonium salts ; a valuable rapid method is thus available for the determination of mercury. The cadmium complex has similar properties, but is slightly soluble in the presence of ammonium salts or in strongly ammoniacal solution ; the experimental details for the determination of cadmium are similar to those given for mercury (Section **IV, 16C**) except that precipitation is effected in *neutral* solution with reagent (*a*) (see below).

The process also permits of a **quantitative separation of copper and mercury.** The acid solution of both metals is treated with ammonia solution until nearly neutral and is then rendered alkaline with ethylenediamine. The solution is heated to boiling, treated with excess of potassium iodide and copper ethylenediamine nitrate solution and allowed to cool ; the mercury complex is filtered off and weighed (Section **IV, 16C**). The copper is determined in another portion of the solution as in Section **IV, 19F.**

The reagent may be prepared by either of the following methods : (*a*) Heat an aqueous solution containing 1 part of cupric nitrate and 2 parts of ethylenediamine on a water bath until a crust forms on the surface of the violet-blue solution. Allow to cool, filter off the separated crystals of $[Cu\ en_2](NO_3)_2,2H_2O$ at the pump, and wash them several times with alcohol, followed by ether. A concentrated solution of this salt is used for precipitations.

(*b*) Treat a solution of cupric sulphate with an aqueous solution of ethylenediamine (5 to 6 times the theoretical quantity) until the dark blue-violet colouration, due to the $[Cu\ en_2]^{++}$ ion, appears and does not increase in intensity upon further addition of ethylenediamine. The presence of excess of the latter in the reagent has no harmful influence. Here the reagent consists of a solution of $[Cu\ en_2]SO_4$, and is as satisfactory as (*a*) for determinations of mercury.

Q. *p*-Hydroxy-phenylarsonic acid. This valuable reagent (XVI), introduced by C. T. Simpson and G. C. Chandlee in 1938, provides a quantitative separation of titanium or zirconium in acid solution from ferrous and ferric iron, chromium, aluminium, beryllium, manganese, zinc, cobalt, nickel, thorium, calcium, thallous thallium, cerous cerium, sodium, potassium and ammonium as well as from phosphate, chromate, permanganate, molybdate, vanadate, uranyl uranium and vanadyl vanadium. The final solution should be about 0·6*N* with respect to hydrochloric acid or 1·8*N* with respect to sulphuric acid. In mineral acid solution of concentration not greater than 0·5*N*, tin is quantitatively precipitated. Thus tin, and also ceric cerium, interfere ; hydrogen peroxide must be absent. The titanium or zirconium complexes are converted by ignition to the oxides, and weighed as such. When both titanium and zirconium are present, the Ti + Zr are first determined as the mixed oxides ; in a second determination use is made of the fact that the zirconium alone is precipitated in the presence of excess of hydrogen peroxide.



(XVI)

The reagent is employed in the form of a 4 per cent aqueous solution.

I, 63. VOLATILISATION OR EVOLUTION METHODS

Evolution or volatilisation methods depend essentially upon the removal of volatile constituents. This may be effected in several ways : (i) by simple ignition in air or in a current of an indifferent gas ; (ii) by treatment with some chemical reagent whereby the desired constituent is rendered volatile ; and (iii) by treatment with a chemical reagent whereby the desired constituent is rendered non-volatile. The volatilised substance may be absorbed in a weighed quantity of a suitable medium when the estimation is a *direct* one, or the weight of the residue remaining after the volatilisation of a component is determined, and the proportion of the constituent calculated from the loss in weight ; the latter is the *indirect method*. Examples of each of these procedures are given in the following paragraphs ; full experimental details will be found in Chapter IV.

The determination of superficially bound moisture or of water of crystallisation in hydrated compounds is usually carried out simply by heating the substance to a suitable temperature and weighing the residue. It is assumed of course that the substance does not decompose upon heating The water may also be absorbed in a weighed quantity of an appropriate drying agent, such as calcium chloride, magnesium perchlorate or concentrated sulphuric acid.

The determination of carbon dioxide in carbonate-containing materials may be effected by treating the sample with excess of acid and absorbing the carbon dioxide in alkaline absorbent, such as soda lime, soda lime-asbestos, or sodium hydroxide-asbestos (" ascarite "). The gas is completely expelled by heating the solution and by passing a current of purified air through the apparatus ; it is, of course, led through a drying agent to remove water vapour before passing to the carbon dioxide absorption apparatus. The gain in weight of the latter is due to carbon dioxide.

In the determination of carbon in steels and alloys, the substance is burnt in pure oxygen in the presence of catalysts and the carbon dioxide absorbed as in the previous example. Precautions are taken to remove other volatile constituents, such as sulphur dioxide. This method is employed in the determination of carbon and hydrogen in organic compounds ; the sample is burnt in a controlled stream of oxygen, and the water and carbon dioxide are absorbed separately in an appropriate absorbent, *e.g.*, in calcium chloride saturated with carbon dioxide and in soda lime (or " sofnolite "—see Section **IV, 76**).

A similar determination is the estimation of ammonia. By heating an ammonium compound with excess of caustic alkali, ammonia is quantitatively evolved and is absorbed in a measured excess of a standard solution of an acid. The excess of the latter is then estimated by titration with standard alkali.

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3.$$

This method may be adapted to the determination of nitrogen in many, but not all, complex organic compounds and to substances containing nitrogen in the organic form. The latter are heated with excess of concentrated sulphuric acid, preferably in the presence of a catalyst such as selenium oxychloride or copper sulphate, whereby the organic nitrogen is converted into ammonium bisulphate. Some potassium sulphate is usually added to raise the boiling point of the acid and thus accelerate the conversion. The acid is then neutralized, and the ammonia liberated with alkali as above. This is the Kjeldahl method for the determination of nitrogen.

Some elements, such as sodium and potassium, may be determined in solution or when combined by evaporating to dryness with sulphuric acid ; the residual sulphate is then weighed.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

Interfering metals must, of course, be removed first.

An example of a related kind is the determination of pure silica in an impure ignited silica residue. The latter is treated in a platinum crucible with a mixture of sulphuric and hydrofluoric acids ; the silica is converted into the volatile silicon tetrafluoride.

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O.$$

The residue consists of the impurities, and the loss in weight of the crucible gives the amount of pure silica present.

ELECTRO-ANALYTICAL METHODS

I, 64. Theory of electro-analysis.—In electro-analysis the element to be determined is deposited electrolytically upon a suitable electrode. Filtration is thus avoided and coprecipitation, if the experimental conditions are carefully controlled, is very rare. The method, when applicable, has many advantages, and we shall therefore study the theory of the process in order to understand how and when it may be applied.

Electro-deposition is controlled by Ohm's law and by Faraday's two laws of electrolysis (1833–34). The latter state :

(1) *The amounts of substances liberated at the electrodes are proportional to the quantity of electricity which passes through the solution.*

(2) *The amounts of different substances which are deposited, or liberated, by the same quantity of electricity are proportional to their chemical equivalents.*

It follows from the second law that when a given current is passed in series through solutions containing, say, copper sulphate and silver nitrate respectively, then the weights of copper and silver deposited will be in the ratio of their equivalents, *viz.*, 107·88 : 63·57/2.

Ohm's law expressed the relation between the three fundamental quantities, current, electromotive force and resistance.

The current C is directly proportional to the electromotive force E and inversely proportional to the resistance R,

$$i.e., C = E/R.$$

Electrical units. The unit of current is called the **ampere.** and is defined as that current which flowing for one second will cause the deposition of 1·11800 milligrams of silver, or 0·3294 milligram of copper, from solutions of their respective salts.

The unit of electrical resistance is the **ohm.** The International ohm is the resistance at 0°C of a column of mercury, of uniform cross section, 106·3 cm. long, and weighing 14·4521 grams.

The unit of electromotive force (e.m.f.) is termed the **volt,** and is the difference of electrical potential required to maintain a current of one ampere through a system having a resistance of one ohm.

The unit quantity of electricity is the **coulomb,** and is defined as the quantity of electricity passing when one ampere flows for one second. Each coulomb will deposit 1·11800 mg. of mercury, or 0·3294 mg. of copper.

The weight of an element liberated by the passage of one coulomb of electricity (or one ampere for one second) is called the **electrochemical equivalent** of the element. The equivalent weight of silver is 107·88, hence 107·88/0·0011180, *i.e.*, 96,494 coulombs will be required to liberate one gram equivalent of silver. The value generally employed is 96,500 coulombs, and this is termed a **faraday** (F). The second law of electrolysis may be stated in the form that one faraday of electricity will liberate one gram equivalent of any substance at each electrode.

I, 65. Decomposition potential.—If a small voltage of, say, 0·5 volt is applied to two smooth platinum electrodes immersed in a solution of molar sulphuric acid, then an ammeter placed in the circuit will at first show that an appreciable current is flowing. Its strength, as shown by the ammeter, decreases rapidly and after a short time becomes virtually equal to zero. If the applied voltage is gradually increased, there is a slight increase in the current until, when the applied voltage reaches a certain value, the current suddenly increases rapidly with increase in the e.m.f. It will be observed, in general, that at the point at which there is a sudden increase in current bubbles of gas commence to be freely evolved at the electrodes. The experiment may be carried out by means of the apparatus shown diagrammatically in Fig. 1-28. A storage battery **C** is connected across a uniform resistance wire **AB**, along which a contact maker **D** can be moved; the fall of potential between **A** and **D** can thus be varied gradually. Two smooth platinum electrodes are immersed in molar sulphuric acid in the cell **E**. **V** is a suitable voltmeter placed between the two electrodes across the cell; **M** is a milli-ammeter and **F** is a switch. When the sliding contact is near to **A**, only a small potential is applied to the electrodes of the cell; the fall of potential across the cell and the current flowing through it are read off on the instruments **V** and **A** respectively. The applied voltage is slowly increased by moving **D** towards **B**, and the readings in the voltmeter and ammeter noted after allowing a short time for the values to become steady. Upon plotting the current against the applied voltage, a curve similar to that shown in Fig. 1-29 is obtained; the point **D** at which the current suddenly increases is clearly shown, and in the instance under consideration is about 1·7 volts. The voltage at the point **D** is termed the **decomposition potential** and it is at this point that the evolution of both hydrogen and oxygen in the form of bubbles is first observed. We may define the **decomposition potential** of an electrolyte as the minimum external voltage that must be applied in order to bring about continuous electrolysis.*

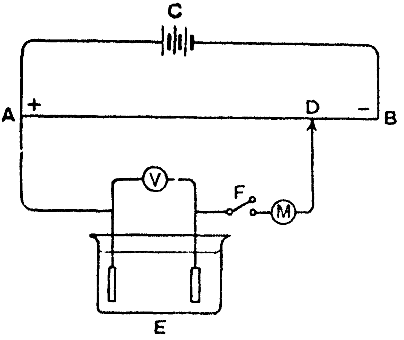


FIG. 1-28.

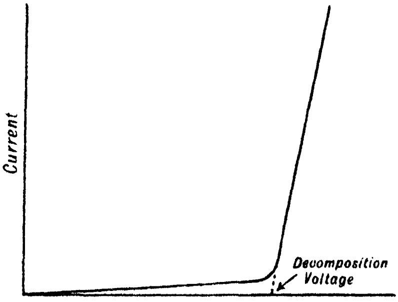


FIG. 1-29.

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* Strictly speaking, the voltage across the cell, measured by the voltmeter **V**, is greater than the decomposition potential by the quantity cr, where c is the current flowing in amperes and r is the resistance in ohms. However, since c is very small and r is not very large, the quantity cr may be neglected, and the voltage measured on **V** taken as the decomposition potential.

If the current is broken after the e.m.f. has been applied, it will be observed that the reading on the voltmeter **V** is at first fairly steady and then decreases, more or less rapidly, to zero. The cell **E** is clearly behaving as a source of current and is said to exert a **back or counter or polarisation e.m.f.,** since the latter acts in a direction opposite to that of the applied e.m.f. This back e.m.f. arises from the accumulation of oxygen and hydrogen at the anode and cathode respectively ; two gas electrodes are consequently formed and the potential difference between them opposes the applied e.m.f. When the primary current from the battery is shut off, the cell produces a moderately steady current until the gases at the electrodes are either used up or have diffused away ; the voltage then falls to zero. This back e.m.f. is present even when the current from the battery passes through the cell and accounts for the shape of the curve in Fig. 1-29. It is evident that the minimum value of the counter e.m.f. may be computed for it is equal to the algebraic difference of the electrode potentials which exist at the anode and cathode respectively. This calculation will be referred to again in the succeeding paragraphs.

Some results of decomposition potential measurements, made by Le Blanc in 1891–93, are collected in Table XXI.

TABLE XXI. DECOMPOSITION VOLTAGES OF *N*-SOLUTIONS BETWEEN SMOOTH PLATINUM ELECTRODES.

Substance	*Decomp. Voltage*	*Substance*	*Decomp. Voltage*
$ZnSO_4$	2·35	$NiCl_2$	1·85
$NiSO_4$	2·09	$ZnBr_2$	1·80
$CdSO_4$	2·03	$CoCl_2$	1·78
$Cd(NO_3)_2$	1·98	$Pb(NO_3)_2$	1·52
$CoSO_4$	1·92	$AgNO_2$	0·70
$CdCl_2$	1·88		
HNO_3	1·69	HBr	0·94
H_2SO_4	1·67	HI	0·52
H_3PO_4	1·70	NaOH	1·69
$HClO_4$	1·65	KOH	1·67
HCl	1·31	NH_4OH	1·74

It will be observed that whereas the decomposition potentials of salt solutions vary considerably, those for the acids and alkalis, with the exception of the halogen acids, are all approximately 1·7 volts. It was therefore concluded that the same electrolytic process occurs with these acids and bases; this can only be the discharge of hydrogen and hydroxyl ions at the cathode and anode respectively leading to the liberation of hydrogen and oxygen.

$$2H^+ + 2\epsilon \rightleftharpoons H_2.$$

$$2OH^- \rightarrow 2\epsilon + 2OH \rightarrow H_2O + 1/2O_2.$$

With the halogen acids in *N* solution, the halogen and not oxygen is liberated at the anode since the discharge of the halogen can occur more readily than the hydroxyl ions.

I, 66. Electrode reactions.—In electro-analysis we are largely concerned with the electrolysis of salt solutions, and it is therefore proposed to study the reactions which take place at the electrodes in some detail. Let us consider the electrolysis of a molar solution of zinc bromide between smooth platinum electrodes. The application of a voltage will result in the deposition of zinc on the cathode (thus producing a zinc electrode) and bromine at the anode (thus producing a bromine electrode). The reaction at the cathode is:

$$Zn^{++} + 2\epsilon \rightleftharpoons Zn,$$

i.e., an oxidation (Section **I, 23**), and that at the anode is:

$$2Br^- \rightleftharpoons Br_2 + 2\epsilon,$$

i.e., a reduction. Thus oxidation occurs at the cathode and reduction at the anode. We may calculate the potential at the cathode at 25°C from the formula (Section **I, 43**):

$$E_{cathode} = E^\circ_{Zn} + \frac{0{\cdot}0591}{2} \log [Zn^{++}] = E^\circ_{Zn},$$

since $[Zn^{++}] = 1$. At the anode:

$$E_{anode} = E^\circ_{Br_2} - \frac{0{\cdot}0591}{1} \log [Br^-] = E^\circ_{Br_2},$$

since $[Br^-] = 1$. The e.m.f. of the resultant cell will therefore be:

$$E^\circ_{Zn} - E^\circ_{Br_2} = 0{\cdot}76 - (-1{\cdot}07) = 1{\cdot}83 \text{ volts}.$$

This value is in agreement with the observed decomposition potential (see Table XXI).

For a similar electrolysis of normal zinc sulphate solution, the reaction at the anode is:

$$2OH^- \rightarrow H_2O + 1/2O_2 + 2\epsilon,$$

for the hydroxyl ion is more easily discharged than the sulphate ion. An oxygen electrode is thus produced at the anode. The potential of a reversible oxygen electrode is a function of the *p*H of the solution, and has been shown to be given by the expression :

$$E = E^\circ_{O_2} + 0{\cdot}0591 \log [H^+].$$

$E^\circ_{O_2}$ is 1·23 volts, and the oxygen potential of a solution normal with respect to hydrogen ions is accordingly 1·23 volts.

In general, it may be stated that the theoretical back or polarisation e.m.f. E_b is given by :

$$E_b = E_{cathode} - E_{anode},$$

where $E_{cathode}$ and E_{anode} are calculated as already described (Section **I, 43**).

I, 67. Overvoltage.—It has been found by experiment that the decomposition voltage of an electrolyte varies with the nature of the electrodes employed for the electrolysis and is, in many instances, higher than that computed from the difference of the *reversible* electrode potentials. The excess voltage over the calculated back e.m.f. is termed the **overvoltage.** The overvoltage may occur at the anode as well as at the cathode. The decomposition voltage E_D is therefore :

$$E_D = E_{cathode} + E_{o.c.} - (E_{anode} + E_{o.a.}),$$

where $E_{o.c.}$ and $E_{o.a.}$ are the overvoltages at the cathode and anode respectively.

The overvoltage at the anode or cathode is a function of the following variables :

1. The nature and the physical state of the metal employed for the electrodes.

2. The physical state of the substance deposited. If it is a metal, the overvoltage is usually small ; if it is a gas, such as oxygen or hydrogen, the overvoltage is relatively great.

3. The current density employed.* For current densities up to 0·01 amp./cm.^{2}, the increase in overvoltage is very rapid ; above this figure the increase in overvoltage continues, but less rapidly.

4. The change in concentration, or the concentration gradient, existing in the immediate vicinity of the electrodes ; as this increases, the overvoltage rises. The concentration gradient depends upon the current density, the temperature and the rate of stirring of the solution.

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* The current density, C.D., is defined as the current per unit area of electrode surface. It is generally expressed in amperes per square centimeter ND_1, or per square decimeter (100 sq. cms.), ND_{100}.

As a rule, metals exhibit small overvoltage effects. Oxygen shows an overvoltage of about 0·45 volt at the anode in acid solution, and is of the order of 1 volt in alkaline solution on a smooth platinum surface with current densities of 0·02 to 0·03 amp./cm.^{2}. The hydrogen overvoltage is of great importance in electrolytic determinations and separations. The values in molar sulphuric acid are shown diagrammatically in Fig. 1-30. In alkaline solutions the hydrogen overvoltage is slightly higher (0·05 to 0·3 volt) than in acid solutions.

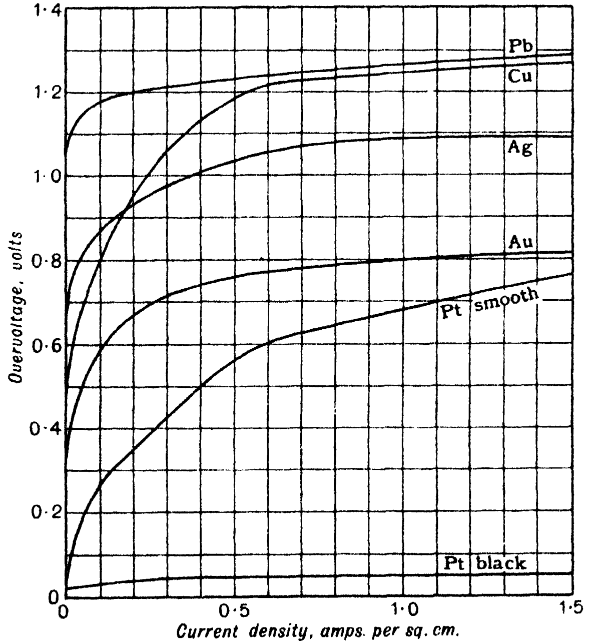

FIG. 1-30.

I, 68. Completeness of deposition.—Let us consider the variations in e.m.f. at the cathode during the deposition of a metal in an electrolytic determination. Let the ionic concentration at the commencement of the estimation be c_i. For a bivalent metal, *e.g.*, copper, the cathode potential at 25°C will be :

$$E^\circ_{M^{II}} + \frac{0{\cdot}0591}{2} \log c = E^\circ_{M^{II}} + 0{\cdot}030 \log c_i \text{ volts.}$$

If the ionic concentration is reduced to one ten thousandth of its original value (*i.e.*, to secure an accuracy of 0·01 per cent in the determination), the new cathode potential will be :

$$E^{\circ}_{M^{II}} + 0{\cdot}030 \log c_i \times 10^{-4} = E^{\circ}_{M^{II}} + 0{\cdot}030 \log c_i + 0{\cdot}030 \log 10^{-4}$$
$$= (E^{\circ}_{M^{II}} + 0{\cdot}030 \log c_i) - 4 \times 0{\cdot}030$$
$$= \text{Potential at commencement of deposition} - 0{\cdot}102 \text{ volt.}$$

This is independent of the value of c_i, and hence whenever the ionic concentration is reduced to one ten thousandth of its initial value (this may be regarded as the ultimate limit of the electro-analytical estimation, although for most purposes an accuracy of 0·1 per cent is regarded as sufficient), the potential is altered by $4 \times 0{\cdot}0591/2 = 0{\cdot}120$ volt for a bivalent ion. For a univalent ion, the change is $4 \times 0{\cdot}0591/1 = 0{\cdot}236$ volt, and for a tervalent ion it is $4 \times 0{\cdot}0591/3 = 0{\cdot}079$ volt. Since the back e.m.f. is produced by a cathode metal acting as the negative pole of a cell, the positive pole being, say, oxygen, it follows that the back e.m.f. will become greater as the metal becomes more negative during the course of the analysis. Otherwise expressed, the decomposition potential increases as the deposition of the metal proceeds. For *quantitative deposition* the applied e.m.f. must equal or exceed the decomposition voltage when the concentration of the given cation is negligibly small (say 10^{-4} of the initial value).

It is important to know the conditions for the deposition of the metal in preference to hydrogen in an electrolysis. The condition for the deposition of the metal is evidently that the potential difference between the electrolyte and the cathode, $E_{solution,\ metal}$, must be less than the reversible deposition of hydrogen plus the overvoltage of hydrogen (o_{H_2}) for the metal under consideration. The relationship may be expressed in several ways :

$$\begin{aligned} E_{solution,\ metal} &< (E_{H^+,H_2} + o_{H_2}), \\ &< (-E_{H_2,H^+} + o_{H_2}), \\ &< (0{\cdot}059\,pH + o_{H_2}) \qquad \text{(at 25°C)}. \end{aligned}$$

If the cathode potential, $E_{metal,\ ion}$, is substituted for $E_{solution,\ metal}$, the expression becomes :

$$E_{metal,\ ion} < (0{\cdot}059\,pH + o_{H_2}).$$

I, 69. Electrolytic separation of metals.—It will be clear from what has been stated in the preceding Section that the initial deposition potentials of two metals must differ by at least 0·25 volt for a virtually quantitative separation to be theoretically possible. This minimum value would require a very precise control of the potential drop at the cathode ; for most practical purposes, the difference in potential should be at least 0·4 volt. From an inspection of Table XXI it is apparent that certain metals can be separated electrolytically with great ease, for example, copper from zinc, nickel, cobalt or lead, silver from copper, etc. When, however, the standard potentials of the two metals differ only slightly, the electro-separation is more difficult. The obvious method is to alter the electrode potential of the one of the metals in some way. This is most simply achieved by decreasing the ionic concentration of the ion being discharged by incorporating it in a complex ion of small instability constant (Section **I, 12**). The decomposition potential of the metal forming a complex ion is thus raised. Furthermore, the overvoltage at the small ionic concentration is also usually increased. A possible consequence of changing the electrode potential in this way is that a metal which in simple ionic solution is liberated at a lower voltage than another metal, may exhibit the reverse behaviour in a complex-forming medium.

Some results, largely due to Foerster (1906), for the deposition potentials ($= - E_{cathode}$) of some metals in simple and alkali cyanide solutions are given in Table XXII.

TABLE XXII. DEPOSITION POTENTIALS E_D OF SOME METALS IN SIMPLE AND IN ALKALI CYANIDE SOLUTIONS.

Metal	E_D *for* 0·1M *solutions of* M^{++} *ions* (*volt*)	*Concentration of Excess of KCN per* 0·1 *Mol of Simple Metallic Cyanide*		
		0·2*M*	0·4*M*	*M*
Zn	+ 0·79	+ 1·03	+ 1·18	+ 1·23
Cd	+ 0·44	+ 0·71	+ 0·87	+ 0·90
Cn	− 0·31	+ 0·61	+ 0·96	+ 1·17

An interesting application of these results is to the direct quantitative separation of copper and cadmium. The copper is first precipitated in acid solution ; the solution is then neutralised with pure aqueous sodium hydroxide, potassium cyanide is added until the initial precipitate just redissolves, and the cadmium is deposited electrolytically. Another application is the simultaneous of zinc and copper (brass) in the presence of molar potassium cyanide.

I, 70. Character of the deposit.—The ideal deposit for analytical purposes should be coherent, dense and smooth ; in this form it is readily washed and the solution rinsed off without loss. Flaky, spongy, powdery or granular deposits adhere only loosely to the electrode, and for this and other reasons should be avoided.

As a rule, more satisfactory deposits are obtained when the metal is deposited from a solution in which it is present as complex ions rather than as simple ions. Thus silver is obtained in a more adherent form from an argentocyanide solution than from silver nitrate solution. Nickel when deposited from solutions containing the complex ion $[Ni(NH_3)_6]^{++}$ is in a very satisfactory state for drying and weighing. Mechanical stirring often improves the character of the deposit since large changes of concentration at the electrodes are reduced, *i.e.*, concentration polarisation is brought to a minimum.

Increased current density up to a certain critical value leads to a diminution of grain size of the deposit. Beyond this value, which depends *inter alia* upon the nature of the electrolyte, the rate of stirring and the temperature, the deposits tend to become unsatisfactory. At sufficiently high values of the current density, evolution of hydrogen may occur owing to the depletion of metal ions near the cathode. If an appreciable evolution of hydrogen occurs, the deposit will usually become broken up and irregular ; spongy and incoherent deposits are generally obtained under such conditions. For this reason the addition of nitric acid or ammonium nitrate is often recommended in the determination of certain metals, such as copper ; bubble formation is thus prevented. The nitrate ion reacts with the hydrogen as it is formed at the cathode :

$$NO_3^- + 10H^+ + 8\epsilon = NH_4^+ + 3H_2O,$$

or

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

For analytical purposes the current densities usually range between 0·1 and 0·5 ampere per square decimeter for electrolysis made in still electrolytes ; somewhat higher values are, however, occasionally employed.

Raising the temperature, say, to between 60°C and 90°C, often improves the physical properties of the deposit. This is due to several factors, which include the decrease in resistance of the solution, increased rate of diffusion, and changed ionisation and overvoltage effects.

In practice, two methods of electrolysis are utilised. In the first method stationary electrodes are used and the solution is not stirred ; small current densities must of necessity be applied in order to secure a coherent deposit, and the procedure is a slow one (**slow electrolysis**). In the second method, which is largely superseding the first, the solution is rapidly stirred (**rapid electrolysis**). Various devices are employed for stirring. An independent mechanical stirrer may be used, but it is more usual to have a rotating anode, which may consist, after Sand, of a platinum wire gauze cylinder surrounded by a similar (but stationary) cylinder, which constitutes the cathode, the intervening space being small (3 to 5 mm.). A very much higher current density may then be applied (ND_{100}, *i.e.*, a current density per 100 sq. cm., of 5 to 10 amps.) without seriously affecting the purity or the physical character of the deposit. The stirring results in a liberal supply of metal ions always being present near the cathode, and consequently the current is principally used in the deposition of the metal or other plate. A considerable saving of time is thus effected, and this accounts for the popularity of the method. It must be emphasised that when the electrolysis is complete, the current must not be switched off as long as the electrodes are in the solution. If the current were broken, the counter e.m.f. would come into play and this would cause part of the metallic deposit to pass back into solution.

I, 71. SEPARATION BY MISCELLANEOUS PHYSICAL METHODS

A. Extraction of solid mixtures by solvents. This method is based upon the dissolution of the desired constituent in some liquid, usually an organic solvent, in which the solubility of any other substances present is so small as to be negligible. Thus in one method for the separation of the alkaline earths, the metals are converted into the anhydrous nitrates, and use is made of the fact that calcium nitrate is soluble whilst strontium and barium nitrates are insoluble in absolute alcohol. After extraction of the calcium nitrate with alcohol, say, in a Sohxlet apparatus, the residue is converted into the chlorides by repeated evaporation with hydrochloric acid.

Strontium chloride may then be extracted with absolute alcohol, and barium chloride remains behind.

Other examples include the separation of lithium chloride from sodium and potassium chlorides by extraction with normal butyl alcohol, amyl alcohol, a mixture of ether and absolute ethyl alcohol, acetone, or dioxan (diethylene dioxide), and the separation of sodium and potassium perchlorates by extraction of the soluble sodium salt with a mixture of equal volumes of ethyl acetate and normal butyl alcohol. Strontium may be separated from calcium by making use of the fact that calcium nitrate is soluble in anhydrous acetone whilst strontium nitrate is insoluble.

B. Extraction of solutions by solvents. Partition or distribution method. A mixture of two substances in a given solvent may often be separated virtually completely if a solvent can be found, which is immiscible with the first, and in which one of the substances is readily soluble and the other practically insoluble. Thus if a mixture of ferric and aluminium chlorides in 6*N* hydrochloric acid be shaken with ethyl ether saturated with hydrogen chloride, the ferric chloride passes largely into the ether layer. By repeating the extraction with fresh portions of ether, the separation may be made practically complete. The results for a number of chlorides are collected in Table XXIII below.

TABLE XXIII. EXTRACTION OF METAL CHLORIDES BY ETHYL ETHER FROM 6*N* HCl SOLUTIONS.

Element	*Per cent extracted at each extraction*	*Element*	*Per cent extracted at each extraction*
Sb ($SbCl_3$)	6	Fe ($FeCl_3$)	99
Sb ($SbCl_5$)	81	Hg ($HgCl_2$)	0·2
As ($AsCl_3$)	68	Mo ($MoCl_3$)	80-90
Cu	0·05	Te ($TeCl_4$)	34
Ga	97	Tl ($TlCl_3$)	90-95
Ge	40-60	Sn ($SnCl_4$)	17
Au ($AuCl_3$)	95	Sn ($SnCl_2$)	15-30
Ir ($IrCl_4$)	5	Zn	0·2
Al, Bi, Be, Ca, Cd, Cr, Co, Fe^{II}, Pb, Mn, Ni, Os, Pd, rare earths, Rh, Ag, Th, Ti, W, U, and Zr are not extracted.			

The ethyl ether extraction method may be employed to separate ferric iron from elements like aluminium, chromium, cobalt, nickel, vanadium, molybdenum and titanium, which accompany it in many alloys. The procedure is to evaporate the hydrochloric acid solution of iron, etc., which should be free from alkali chlorides (these are insoluble in ether-hydrochloric acid) and from substances that decompose ether (chlorine, nitric acid, etc.), to take up the residue with hydrochloric acid (sp. gr. 1·1), and to transfer it with the aid of this acid to a separating funnel. The cold acid solution is extracted three times by shaking with ethyl ether: between each extraction the ether layer is allowed to separate before the lower layer is drawn off for re-extraction. The iron is removed from the ethereal extract by shaking it with water and drawing off the lower aqueous layer. Heat is generated by the mixing of the ether and ferric chloride-hydrochloric acid solution so that cooling the mixture under the tap or in ice is essential. The liberation of heat is considerably reduced by the use of concentrated hydrochloric acid saturated with ether for dissolving the syrupy residue of ferric chloride, etc. (100 ml. of hydrochloric acid, sp. gr. 1·19, dissolve 150 ml. of ethyl ether; if the sp. gr. of the acid is 1·1 only 30 ml. of ether is dissolved).

Improved results are obtained with the less-volatile *iso*propyl ether (R. W. Dodson, F. J. Forney and E. H. Swift, 1936). In particular, the extraction of ferric chloride from aqueous hydrochloric acid solutions is more efficient for a wider range of acid concentration (6·5 to 8·5*N*; the optimum concentration is 7·75 to 8·0*N* and the efficiency is 99·9 per cent after 3 extractions) than for ethyl ether, and furthermore the volume changes of the isopropyl ether and aqueous layers are smaller and no reduction of ferric iron occurs when both isopropyl alcohol and peroxide are present in moderate amounts. Satisfactory separations of iron from copper, cobalt, nickel, manganese, zinc, aluminium, chromium, quadrivalent vanadium, titanium and sulphur (as sulphuric acid) can be obtained. Large amounts of quinquevalent vanadium are extracted; phosphoric acid and hexavalent molybdenum pass into the ether layer with ferric iron.

Gold chloride may also be extracted in a similar manner using ethyl acetate as solvent. An interesting application is to the determination of molybdenum in steel; the brown colouration produced by the formation of molybdenum thiocyanate is extracted with *cyclo*hexanol (see Section **V, 16**).

The theory of the process is as follows. If a solute is shaken with two immiscible solvents, and its molecular state is the same in both, then it has been found that at any given temperature :

$$\frac{\text{Concentration of solute in solvent } A}{\text{Concentration of solute in solvent } B} = \frac{C_A}{C_B} = \text{a constant} = K,$$

where K is the **distribution** or **partition coefficient.** Thus K for iodine distributed between carbon bisulphide (A) and water (B) is about 410 at 18°C. The problem in practice is to determine what is the most efficient method for removing a substance quantitatively from solution. It can be shown* that if W ml. of, say, an aqueous solution containing x_0 grams of a substance be extracted n times with L ml. portions of a given solvent, then the weight of the substance x_n remaining in the water is given by the expression :

$$x_n = x_0\left(\frac{KW}{KW + L}\right)^n$$

where K is the distribution coefficient between *water and the given solvent* (compare Section **I, 60**). It follows, therefore, that the best method of extraction with a given volume of extracting liquid is to employ several fractions of the liquid rather than to utilise the whole quantity in a single extraction.

Let us take a particular example. Let us suppose that we shake 50 ml. of water containing 0·1 g. of iodine with 25 ml. of carbon tetrachloride. The distribution coefficient of iodine between water and carbon tetrachloride at the ordinary laboratory temperature is 1/85, *i.e.*, at equilibrium the iodine concentration in the aqueous layer is 1/85th of that in the carbon tetrachloride layer. We will compute the weight of iodine remaining in the aqueous layer after one extraction with 25 ml. and also after, say, three extractions with 8·33 ml. of the solvent by application of the above formula. The former can also be simply computed as follows. If x_1 g. of iodine remains in the 50 ml. of water, its concentration is $x_1/50$ g. per ml. ; the concentration in the carbon tetrachloride layer will be $(0{\cdot}1 - x_1)/25$ g. per ml. Hence :

$$\frac{x_1 / 50}{(0{\cdot}1 - x_1) / 25} = \frac{1}{85}, \text{ or } x_1 = 0{\cdot}00230 \text{ g.}$$

The concentration in the aqueous layer after three extractions with 8·33 ml. of carbon tetrachloride is given by :

$$x_3 = 0{\cdot}1 \left(\frac{(1/85) \times 50}{(50/85) + 8{\cdot}33}\right)^3 = 0{\cdot}0000145 \text{ g.}$$

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* For derivation, see Taylor, *A Treatise on Physical Chemistry*, 1930, I, p. 487 (Macmillan and Co. Ltd.).

the acceleration due to gravity. Strictly speaking, F_1 and F_2 are the true **weights** in the two pans. But :

$$\frac{F_1}{F_2} = \frac{M_1 g}{M_2 g} = \frac{M_1}{M_2},$$

i.e., the ratio of the forces with which the bodies in the two pans are attracted by gravity is equal to the ratio of the two masses. In quantitative analysis we are interested only in the amount of matter in the body, *i.e.*, in its mass : this is independent of g. At any given place, the weights are proportional to the masses. It has become customary to employ the term " weight " synonymously with the mass, and it is in this sense that " weight " is employed in quantitative analysis. The analytical balance, strictly speaking, determines mass and not weight.

II, 2. Description of a typical analytical balance.—The essential features of a typical analytical balance are shown diagrammatically in Fig. 2–2. The beam, which is constructed

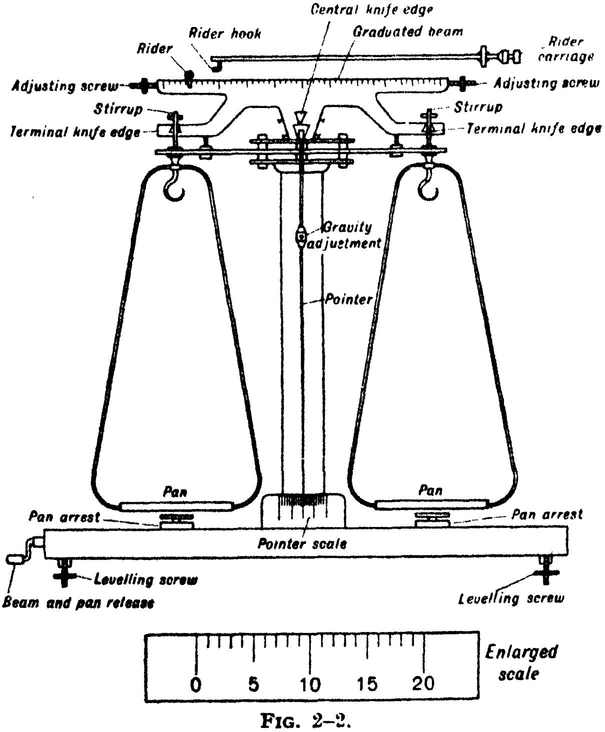

FIG. 2–2.

as rigidly and as light in weight as possible, is mounted at its centre upon a prism-form agate knife edge, which rests upon an agate plate (when the balance is in use) attached to the central beam support. The two terminal agate knife edges, fixed at equal distances from the central knife edge, each support a suspension (stirrup) from which the pans are hung, contact being made upon agate planes fixed to the stirrups. A long pointer is attached to the centre of the beam: this moves over a scale at the foot of the pillar and serves to indicate the deflection of the beam from the horizontal position when the balance is in operation. The balance is levelled with the aid of levelling screws and a plumb line suspended from the column; in some balances a pair of spirit levels are provided. In the Figure the whole of the beam is divided into 100 equal parts so that weight adjustments smaller than 10 mg. can be made readily by moving a small piece of platinum or gold wire (the **rider**) along the beam by means of the rider hook and rider carriage. For the beam graduated as shown in the Figure a 5 mg. rider is employed; in many balances only the right half of the beam is graduated, a 10 mg. rider is then necessary. A small weight is attached to the pointer; this serves to move the centre of gravity and thereby alter the sensitivity of the balance. The adjusting screws at the ends of the beam are employed for the purpose of adjusting the equilibrium position of the pointer so that it rests at the centre of the scale, thereby ensuring that the beam is horizontal when unloaded. In the better type of balances, the sensitivity and equilibrium position of the pointer are adjusted by means of a screw-nut device attached to the centre of the beam behind the rider bar and is shown diagrammatically in Fig. 2-3; the screws at the end of the beam and on the pointer are then, of course, omitted.

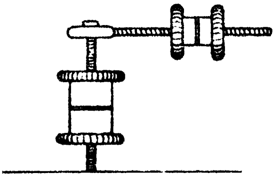
FIG. 2-3.

In order to protect the knife edges from undue wear and from injury during the transfer of weights and objects, the balance is provided with a device whereby the moving parts can be raised so that the knife edges and planes are very slightly separated. This is operated by means of a large screw attached to the base of the balance, placed either centrally in the front of the base as shown in the Figure, or, in some cases, in the centre of the left-hand side of the base. In many balances the beam arrest is combined with the pan arrest; in others, the pan arrest mechanism is separately controlled by a push button (not shown in the Figure).

II, 3. The requirements of a good balance.—These are:

(*a*) *The balance must be accurate and give the same result in successive weighings.*

This requisite is obtained if the arms are of equal length, if the beam is rigid and does not bend appreciably under load, and if all the three knife edges lie in the same plane and are parallel to one another.

(*b*) *The balance must be stable, that is, the beam must return to the horizontal position after swinging.*

This is attained by a proper adjustment of the centre of gravity.

(*c*) *The balance must be sensitive, that is,* 0·1 *mg. should be readily detectable with average loads.*

We may define the **sensitivity of a balance** as the angular deflection α of the beam when a known small weight is added. It can be shown that the angle α is determined by the excess of weight w producing the deflection α, the length of the balance arm d, the weight of the beam W, and the distance between the centre of gravity and the point of support of the beam h. Expressed mathematically*:

$$\tan \alpha = \frac{wd}{Wh}.$$

Since α is small, we may put $\tan \alpha = \alpha$. The angular deflection of the beam is equal to the angular deflection of the pointer, and the latter is directly proportional to the number of divisions between the two points of rest on the scale at the foot of the beam. This leads directly to the usual definition of sensitivity, *viz.*, the **sensitivity**† of a balance is the number of scale divisions that the rest point (or equilibrium point) is displaced by an excess of weight of 1 mg.

It follows from the above expression that: (i) the longer the balance arms, the greater is the sensitivity; (ii) the lighter the beam, the greater is the sensitivity; and (iii) the smaller the distance between the point of suspension of the beam and the centre of gravity, the greater is the sensitivity. These conditions for maximum sensitivity are unfortunately conflicting with one another. Thus long arms are incompatible with minimum weight. The length of the arm is also limited by the fact that the time of swing of the pointer, which must not be excessive, increases with its length. It is also important that the balance beam be rigid in order that the centre of gravity, and therefore the sensitivity, should not change appreciably with the load. The centre of gravity must always be below the central knife edge, otherwise the balance will be in neutral or unstable equilibrium. The sensitiveness may be changed by moving the small weight attached to the pointer or, in some balances, by rotation of the nut on the screw attached to the central portion of the beam, which affect the position of the centre of gravity. In general, a balance adjusted to give a deflection of 3 to 4 scale divisions per milligram is quite satisfactory for quantitative work.

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* For deduction, see H. A. Fales, *Inorganic Quantitative Analysis*, 1928, p. 81 (Century).

† Also termed sensibility and sensitiveness.

(*d*) *The period of oscillation should be short.*

This is necessary in order that weighings can be made rapidly. For this reason " short-arm " balances, which have a period of swing of 5 to 10 seconds, are almost universally employed in analytical practice. The so-called " long-arm " balances, although more sensitive, have a long time of swing (about 15 seconds) which renders weighing a tedious process.

Sensitivity and maximum load of a balance. In an ideal balance, free from friction and with a perfectly rigid beam, the sensitivity would be independent of the load. Most balances, however, exhibit a decreasing sensitivity with increasing load, and this change of sensitivity provides a good criterion as to the maximum safe load that a balance can carry. The criterion is : no greater load should ever be placed upon the balance pans than the load at which the sensitivity becomes forty per cent of its maximum value (see Section **II, 6A** and Fig. 2-4).

II, 4. Weights. Reference masses.—The determination of the mass of an object with an equal-arm balance necessitates the use of a series of reference masses termed **weights.** For scientific work, the international metric system of weights and measures is employed. The fundamental standard of mass is the **international prototype kilogram,** which is a mass of platinum-iridium alloy made in 1887 and deposited in the International Bureau of Weights and Measures near Paris. It represents as closely as possible the mass of 1000 grams of water at the temperature of its maximum density (4°C). Authentic copies of the standard are kept by the appropriate responsible authorities* in the various countries of the world ; these copies are employed for the comparison of secondary standards, which are used in the calibration of weights for scientific work. The unit of mass that is almost universally employed in laboratory work, however, is the **gram,** which may be defined as the one thousandth part of the mass of the international prototype kilogram.

Multiples and sub-multiples of units in the metric system are indicated by the following prefixes :

kilo = a thousand times ; *milli* = a thousandth part, or 0·001 ;
hecto = a hundred times ; *centi* = a hundredth part, or 0·01 ;
deca = ten times ; *deci* = a tenth part, or 0·1.

The following weights are frequently encountered : kilogram (kg.), decigram (dg.), centigram (cg.), and milligram (mg.).

An ordinary set of analytical weights contains the following : Grams : 100, 50, 20, 10, 10, 5, 2, 1, 1, 1 (or 5, 2, 2, 1). Milligrams : 500, 200, 100, 100, 50, 20, 10, 10, 5, 2, 2, 1. Weights smaller than 10 mg. are not actually used in weighing, and are therefore not really essential. In addition to the weights, a set includes two " riders," which are small weights of 5 or 10 mg. denomination, made of platinum, gold, or aluminium wire, for use on the beam of the balance. The weights from 1 gram upwards are generally constructed of polished brass ; these are often plated with gold or platinum to avoid corrosion. Recently weights of stainless steel have been introduced. The fractional weights, from 0·5 g. downwards, are made of platinum, gold, aluminium or tantalum ; they are usually square in shape and have one corner turned up to facilitate handling. The nominal mass is stamped on each weight, the numbers indicating grams, fractions of a gram or milligrams. Duplicate and triplicate weights are stamped with one or two asterisks. For handling the weights, a pair of forceps, frequently tipped with ivory or some similar material, is provided : on no account should weights be touched with the fingers.

All weights should be calibrated (Section **II, 8**). The values may change with time, and it is advisable to recalibrate the weights at least once a year.

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* The National Physical Laboratory (N.P.L.) in Great Britain, the Bureau of Standards in U.S.A., etc.

II, 5. Care and use of the balance.—*1.* The balance should be placed upon a firm foundation, which is as free from mechanical vibration as possible. The ideal foundation is a concrete or stone slab resting upon brick piers, which are either sunk into the ground or, if this is not practicable, into the stone or concrete flooring beneath the floor boards of the laboratory. If this is not possible, the balance should be placed upon a stout table or shelf and protected, when necessary, by shock absorbing media, such as cork mats or sheet rubber under the table. It is best to keep the balance in a room separate from the laboratory in order to protect it from fumes. Its position should be such that the two arms are at the same temperature. Hence the balance should not be placed with one side near a window or radiator, or in direct sunlight, or in a position where it is likely to come into contact with draughts.

The balance should be level. This adjustment may be made with the aid of the levelling screws.

2. When not in use, the balance beam and the pan supports should be raised so as to protect the agate prisms and planes. The doors of the balance should be kept closed as much as possible.

3. To release the balance, the beam and pans should be lowered very carefully and set swinging by fanning one pan gently with the hand, or by carefully turning the arresting screw. The beam should never be set swinging by touching the pan with the forceps or with some other object, or by suddenly lowering it upon its prism edges.

4. Objects to be weighed must be allowed to attain the temperature of the balance before weighing is attempted, otherwise the air currents produced inside the balance case may introduce serious errors. If the object has been heated, sufficient time must be allowed for cooling. The time required to attain the balance room temperature varies with the size, etc., of the object, but as a rule thirty to forty minutes is sufficient.

5. Weights and the object to be weighed should always be placed in the centre of the pans.

6. During a weighing or upon any occasion when objects are being added to or removed from the pans, both the beam arrests and the pan supports must be raised so as to protect the prism-edges from injury. Always close the balance case when starting to use the rider.

7. No chemicals or objects which might injure the balance pans should ever be placed directly upon them. Substances must be weighed upon suitable containers, such as watch glasses, small beakers, weighing bottles or crucibles. Liquids and volatile or hygroscopic solids must be weighed in a tightly closed vessel, such as a stoppered weighing bottle.

8. The balance must not be overloaded (see Section **II, 3, d**).

9. Weights should be handled only with the forceps provided with the box.

10. Nothing must be left on the pans when the weighing has been completed. If any substance is spilled accidentally upon the pans or upon the floor of the balance case, it must be removed at once. The pans should be lightly brushed periodically with a camel-hair brush to remove dust which may have collected.

11. If the balance requires adjustment, the teacher should be notified immediately.

II, 6. METHODS OF WEIGHING.

There are three methods of weighing, *viz.*,

(*A*) Direct weighing.
(*B*) Gauss's methods of double weighing.
(*C*) Borda's method of substitution.

Of these, method *A*, in one of its various modifications, is most widely employed in quantitative analysis. It will therefore be discussed in some detail.

(A) Direct weighing. The object is placed on the left-hand balance pan and weights are added to the other pan until the beam returns to its original equilibrium position. The modifications of this method differ only in the procedure for determining the equilibrium position of the beam.

(i) Weighing by point of rest and sensitivity. The first step in any method of weighing is the determination of the equilibrium position of the beam when the pans are unloaded. The position of the beam is of course indicated by the position of the pointer on the scale. We shall call the equilibrium position **the zero point** when the pans are empty, and **the point of rest** when the pans are loaded.

Determination of the zero point. See that the balance is level; if necessary, turn the levelling screws at the base until the balance is suitably adjusted (spirit level or plumb-line). Note also whether the prism edges are in proper position with respect to their bearings, and also whether the pans are free from dust (the latter can be removed, if necessary, by means of a camel-hair brush). The rider should be placed on the zero graduation if the whole of the beam is graduated ; if only the right half of the beam is graduated, the rider should be removed from the beam. The beam and pan arrests are lowered very carefully, and the beam set swinging either by fanning one pan gently with the hand or, more usually, by careful manipulation of the arresting control. The doors of the balance are then closed.

The pointer scale may be regarded as being graduated as shown in Fig. 2–2, *i.e.*, numbered from zero to twenty. It is convenient to have the pointer swinging about 5 to 6 divisions on either side of the centre mark (10) of the scale. The beam is allowed to make two or three swings, and then readings are taken to the nearest tenth of a division of the extreme positions of the pointer. An odd number of swings, usually three, is taken on the left-hand side and even number, usually two, on the right-hand side. The eye of the observer should remain in the same position to avoid errors due to parallax. The two sets of observations are averaged separately, and the mean of their average taken. This mean value is the **zero point.*** The procedure is best made clear with the aid of an example. Five successive readings of the pointer might be :

	Left		*Right*
	(i) 5·3		(i) 15·2
	(ii) 5·7		(ii) 14·9
	(iii) 6·0	Average	15·1
Average	5·7		

Mean = (5·7 + 15·1) / 2 = 10·4 = *zero point.*

After some practice, the zero point may be calculated from three successive readings of the extreme positions instead of five. If the zero point lies outside the positions 9 and 11, *i.e.*, more than one division from the centre line of the scale, the student should ask the teacher to make an adjustment on the nuts attached to the ends of the beam or, for some balances, on the nuts upon a small lever attached to the centre of the beam.

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* For a mathematical justification of this procedure, see H. A. Fales, *Inorganic Quantitative Analysis*, 1928, p. 85. It must be realised that the beam swings about the prism edge like a compound pendulum and that the oscillations are damped, or shortened, by the friction in the bearings and by air resistance ; consequently each swing will be slightly less in amplitude than the preceding one.

The next step is the determination of the sensitivity of the balance.

Determination of the sensitivity of the balance. The sensitivity of a balance depends *inter alia* upon the distance between the centre of gravity and the point of suspension of the beam (Section **II, 3**). Since most beams are not perfectly rigid, the distance, and consequently the sensitivity, will change with the load. Whether the sensitivity increases or decreases with increase of load depends upon the relative positions of the beam prism-edge and the pan prism-edges. The **sensitivity** has already been arbitrarily defined as the number of scale divisions that the point of rest is displaced by an excess of weight of one milligram.*

The pans and beam are arrested and the rider is placed exactly on the 1 mg. graduation of the beam. The beam is then set swinging and the rest point determined exactly as described above. Thus, if the zero point is 10·4 and the rest point with a load of 1 mg. is 6·3, then the sensitivity at this load is 1 mg. = 4·1 scale divisions, and the displacement of one division corresponds to 0·0010/4·1 = 0·0002 g. The sensitivity for a load of 10 grams is obtained by placing 10 g. in each pan and determining the rest point; the rider is displaced 1 mg. and the rest point again determined. The difference gives the sensitivity. Similar estimations are made for loads on each pan of 30, 40, 50, and 100 g. The results may then be plotted as shown in Fig. 2–4. The sensitivity at any load can then be found by reference to the curve. Alternatively, a table may be constructed showing the sensitivity at various loads, and also the number of mg. corresponding to one scale division. Either the

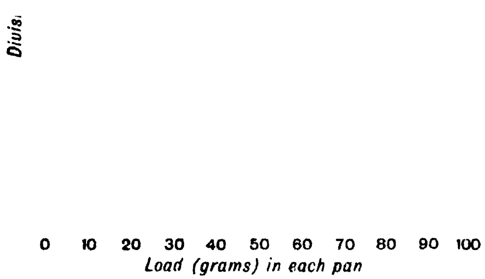

FIG. 2-4.
Sensitivity Curve of a balance.

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* An alternative definition which is sometimes employed is the following: the sensitivity is the weight necessary to shift the equilibrium position of the pointer by one scale division.

graph or the table should be placed in a conspicuous position in the balance case.

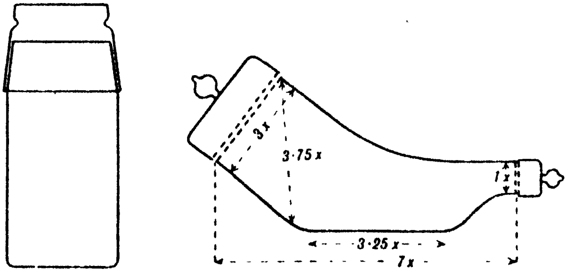
Weighing by the method of swings. Having determined the zero point and the sensitivity at various loads, the actual weighing operation may be performed. The object is placed on the left-hand pan and weights are added to the right-hand pan in systematic order. The beam and pans should be raised before an object or a weight is placed on the pans. A weight estimated to be slightly heavier than the object is removed from the box with the forceps and placed in the centre of the right-hand pan. The beam is lowered just enough to see which way the pointer moves; the beam is then raised. If the weight is too heavy, it is removed and the next smaller weight substituted for it. If the latter is too light, it is allowed to remain on the pan and the next lower weight added. This process is repeated in a systematic order until the gram weight is reached. The fractional weights are similarly added in order of decreasing denomination down to and including the 10 mg. weight. Here, particularly in the concluding stages, it will be necessary to lower the beam and pans completely in order to detect the inequality.

The final adjustment is made with the rider with the balance case closed. For very accurate weighing, the rider is adjusted to the nearest mg. and the tenths (or hundredths) of a milligram are then calculated from the difference between the zero point and the rest point, the sensitivity being known for the load on the pans. An example will make the method of calculation clear. A certain object is found to weigh between 12·673 g. and 12·674 g. The rider is then placed exactly on division 3 (mg.) and the rest point determined by the method of swings. Suppose this is 12·4. The zero point is, say, 10·4. The sensitivity of the balance, estimated from the sensitivity-load graph, is 3·8 divisions per mg. The weight is therefore:

$$12{\cdot}673 + (12{\cdot}4 - 10{\cdot}4) \times 0{\cdot}001/3{\cdot}8 = 12{\cdot}673 + 0{\cdot}00053$$
$$= 12{\cdot}67353 \text{ g. or } 12{\cdot}6735 \text{ g. (to the nearest } 0{\cdot}1 \text{ mg.).}$$

(ii) **Weighing by the method of short swings.** For ordinary analytical work, entirely satisfactory weighings to an accuracy of 0·1 mg., can be made by the method of short swings. The swings observed are so short that the damping effect produced in two successive swings is inappreciable. The zero or rest point is determined by adding together the observed values of two successive swings on either side of the centre of the pointer scale, and taking the mean. The swings may vary from 4 divisions on the pointer scale to the shortest one that is distinctly visible; those from 1 to 2 divisions on either side of the centre of the scale are usually satisfactory. As an example, we may consider two successive swings + 2·2 and − 2·0; the centre of the scale is here taken as the reference point, values to the right being positive and those to the left negative. The zero point is $(+ 2{\cdot}2 + - 2{\cdot}0)/2 = + 0{\cdot}1$. This method of weighing is recommended for all routine work, but is not suitable for the calibration of weights (see Section **II, 8**).

(iii) **Weighing of chemical samples.** It will be convenient at this stage to discuss the application of the two methods of direct weighing just described to the weighing of chemical samples. Most chemicals are weighed by *difference* in order to avoid exposing the sample to the atmosphere, from which dry substances may absorb moisture in varying amounts. If the sample has been dried, it should be placed in a weighing bottle and kept in a desiccator, containing a suitable drying agent, until required for weighing. The most convenient form of weighing bottle is that provided with a ground-on cap (Fig. 2–5*a*). That with a ground-in stopper is not recommended particularly for weighing powders; there is always a danger that the small particles may adhere to the ground surface and that when the stopper is pressed into place, they may either tend to cause the stopper to stick or else be forced out and lost. A special type of "**duplex**" **weighing bottle,** together with the relative dimensions, is shown in Fig. 2–5*b*. This is fitted with externally ground caps, and possesses many obvious advantages. Among these may be mentioned



(*a*) (*b*)

FIG. 2–5.

the flattened side which gives great stability, the wide mouth which permits facile addition and removal of solids, the narrow mouth which allows of easy transfer of solids or liquids into narrow-neck receptacles, and finally the designed slopes which permit easy access of brush or stream of liquid into and against all parts of the interior.

To weigh a substance by difference, weigh a glass-stoppered weighing bottle (Fig. 2–5*a*) containing the sample. Approximately the desired amount is then transferred into a suitable container (beaker, flask, etc.) by appropriate shaking, and the bottle reweighed. If desired, the sample may be removed with the aid of a small clean spatula (which should preferably be of platinum) which is kept in the bottle. Sometimes the sample is removed with the aid of a clean spatula, spoon or scoop, which is not weighed ; it is then of the greatest importance that every particle removed from the bottle be transferred to the container. The spatula or scoop should be carefully brushed with a small camel-hair brush.

In the actual transfer of the weights from the box to the balance pan, it is desirable to place the gram weights in the centre of the pan, the decigram weights to one side and the centigram pieces to the other side. This will assist in reducing the likelihood of error in recording the weighing. The weights on the pan are noted and their values confirmed by observing the vacant places in the weight box. As a final check, the value of each weight as it is returned to the box is noted. All weights should be recorded in ink in a note book at the time that they are made : loose sheets of paper should never be used as they are readily lost.

If the sample is unaffected by exposure to the air, it may be weighed on a watch glass. A clean, dry watch glass is weighed ; portions of the sample, which should preferably be in the form of a powder, are added by means of a spatula or scoop until the weight is approximately correct, and the combined weight is then determined. It is often convenient to have a pair of counterpoised watch glasses for this purpose, *i.e.*, a pair of watch glasses which weigh so nearly the same that they can be balanced with the aid of the rider alone. One watch glass is placed on each pan, and weights are placed on the right-hand pan amounting to the desired quantity of the sample ; the latter is then added with a spatula or similar apparatus.

Liquids must be weighed in closed weighing bottles. The most convenient method is to weigh the empty bottle and stopper; the approximate amount of liquid is introduced by a graduated pipette or glass tube, and the bottle is reweighed. The entire contents of the bottle is then washed into the second container.

Sometimes ignited precipitates are hygroscopic or tend to absorb carbon dioxide from the air. Weighing must then be made as rapidly as possible. These precipitates are ignited to constant weight; the approximate weight is therefore known from a previous ignition. In the final weighing it is perhaps best to adjust the rider to the nearest milligram and then to determine tenths of a milligram by the method of swings.

An experimental point which merits attention is that a vessel should always be weighed filled with the same gas. Thus in the determination of carbon by combustion in oxygen and the absorption of the resultant carbon dioxide in a U-tube containing soda lime or some other substance, it is important to weigh the absorption tube filled with air both before and after the determination. To get some idea of the error resulting from the neglect of this precaution, let us take the case of a U-tube of, say, 50 ml. capacity. One litre of air at 20°C and 760 mm. pressure weighs approximately 1·20 g., and one litre of oxygen under similar conditions weighs 1·33 g. The difference in weight produced by substituting oxygen for air will be $(1{\cdot}33 - 1{\cdot}20) \times 50/1000$, or 0·0065 g. Since the weight of carbon dioxide absorbed is usually of the order of 0·1 g., the neglect of this precaution will introduce an error of about 6·5 per cent.

A common procedure in quantitative analysis is to dissolve a known weight of a substance in a definite volume of liquid, which is usually distilled water or distilled water to which a reagent has been added. A graduated flask is generally employed for this purpose. The operation is carried out as follows. Insert a short-stemmed funnel into the neck of the flask. Transfer the required amount of substance from the weighing bottle to the funnel, taking care that no particles are lost. After the weighing bottle has been reweighed, the substance in the funnel is washed down with a stream of the liquid. The funnel is thoroughly washed, inside and out, and then removed from the flask; the contents of the flask are dissolved, if necessary, by shaking or swirling the liquid, and then made up to the mark, if an exact volume is required. If a watch glass is employed for weighing out the sample, the contents are transferred as completely as possible to the funnel; the last traces remaining on the watch glass are transferred by washing. The procedure is then as above.

B. Gauss's method of double weighing. This method will eliminate any errors due to the inequality of the arms. Let us suppose that the lengths of the arms are d_1 and d_2 respectively (see Fig. 2–1), and the true mass of the object is M_t. If the object is placed in the left-hand pan and is counterbalanced by weights W_r on the right-hand pan, we have by the principle of moments:

$$M_t \times d_1 = W_r \times d_2 \qquad \text{(i).}$$

If now the object is placed in the right-hand pan and is counterbalanced by weights W_l on the left-hand pan, we have:

$$M_t \times d_2 = W_l \times d_1 \qquad \text{(ii).}$$

Upon multiplying these two expressions together and cancelling out the common factor d_1d_2, we obtain:

$$M_t^2 = W_rW_l, \text{ or } M_t = \sqrt{W_rW_l} \qquad \text{(iii),}$$

i.e., the mass is equal to the square root of the product of the two apparent weights. Since d_1 and d_2 are very nearly equal, it is sufficiently accurate to write:

$$M_t = (W_r + W_l)/2 \qquad \text{(iii}'\text{),}$$

i.e., the true mass is equal to the arithmetic mean of the apparent weights.

C. Borda's method of weighing. This is another method for determining the true mass of an object; it is independent of the inequality of the balance arms. The object is placed on the right-hand pan, and counterbalanced or **tared** by any convenient counterpoise, which may be the weights of a duplicate set, lead shot or sand. The rest point of the balance is determined. The object is then removed and replaced by weights which give the same rest point. The mass of the object is thus equal to the mass of the weights on the left-hand pan. This method is useful for weighing large objects. It is also employed in the calibration of weights, but the precision is not so great as in Gauss's method.

II, 7. Errors in weighing.—The chief sources of error are the following:

1. Change of the condition of the containing vessel or of the substance between successive weighings.

2. Inequality of the lengths of the balance arms.

3. Effect of the buoyancy of the air upon the object and the weights.

4. Inaccuracy of the weights.

The first source of error is occasioned by the change in weight of the containing vessel (*a*) by absorption or loss of moisture, (*b*) by electrification of the surface caused by rubbing, and (*c*) by its temperature being different from that of the balance case. These errors may be largely eliminated by wiping the vessel gently with a linen cloth, and allowing it to stand at least 30 minutes in the balance room before weighing. The electrification, *which may cause a comparatively large error particularly if both the atmosphere and the cloth are dry*, is slowly dissipated on standing, but is best removed by placing a piece of pitchblende or other radioactive material in the balance case to ionise the air. The best method, if practicable, is to use a vessel of similar dimensions as a tare. Hygroscopic, efflorescent, and volatile substances must be weighed in completely closed vessels. Substances which have been heated in an air oven or ignited in a crucible must be allowed to cool in a desiccator containing a suitable drying agent. The time of cooling in a desiccator cannot be exactly specified, since it will depend upon the temperature and the size of the crucible as well as upon the material of which it is composed. Platinum vessels require a shorter time than those of porcelain, glass or silica. As a general rule, platinum crucibles should be left in the desiccator for 25 minutes, and crucibles of other materials for 35 to 40 minutes before being weighed.

The use of drying agents or absorbents for carbon dioxide in the balance case is generally of little value except where atmospheric conditions are such as to otherwise cause serious corrosion of the balance. These reagents give comparatively little protection during weighing, for the small surface of absorbent usually exposed cannot quickly purify the air introduced when the case is opened. However, if reagents are to be used, soda-lime and fused calcium chloride are satisfactory.

The error due to the inequality of the lengths of the balance arms may be completely eliminated by Gauss's method of double weighing (Section **II, 6B**) or by Borda's method of substitution (Section **II, 6C**). In a good analytical balance the arms will seldom differ in length by more than 1 part in 50,000 so that the error introduced by the direct method of weighing is not large. The error is still further reduced in routine work in quantitative analysis where the sample and the ignited or dried precipitate is weighed on the same balance and on the same pan. Here absolute weights are not essential, since it is only the ratio of the weights with which we are concerned. It is clear that it both the sample and the precipitate are both affected by the same small error, the ratio of the weights will not be appreciably affected. Where absolute weights are required, as in the calibration of weights or of volumetric apparatus, one of the two methods mentioned at the beginning of this paragraph must be used.

Effect of the buoyancy of the air. Reduction of weighings to vacuo. When a substance is immersed in a fluid, its true weight is diminished by the weight of the fluid which it displaces. If the object and the weights have the same density, and consequently the same volume, no error will be introduced on this account. If, however, as is usually the case, the density of the object is different from that of the weights, the volumes of air displaced by each will be different. If the substance has a lower density than the brass weights, as is usual in analysis, the former will displace a greater volume of air than the latter and it will therefore weigh less in air than in a vacuum. Conversely, if a denser material (*e.g.*, one of the precious metals) is weighed, the weight in a vacuum will be less than in air.

Let us enquire into the magnitude of the error. First, let us consider the weighing of a litre of water, first " in vacuo," and then in air. It is assumed that the flask containing the water is tared by an exactly similar flask, that the temperature of the air is 20°C and the barometric pressure is 760 mm. of mercury. The weight of 1 litre of water " in vacuo " at 20°C and 760 mm. is 998·23 grams. If the water is weighed in air, it will be found that 998·23 grams are too heavy. We can readily calculate the difference. The weight of 1 litre of air displaced by the water is 1·20 grams. The brass weights have a density of 8·4, hence they will displace $998{\cdot}23/8{\cdot}4 = 116{\cdot}9$ ml., or $116{\cdot}9 \times 1{\cdot}20/1000 = 0{\cdot}14$ grams of air. The net difference in weight will therefore be $1{\cdot}20 - 0{\cdot}14 = 1{\cdot}06$ grams. Hence the weight in air of 1 litre of water under the experimental conditions named is $998{\cdot}23 - 1{\cdot}06 = 997{\cdot}17$ grams, a difference of 0·1 per cent from the weight " in vacuo."

Let us now extend our enquiry to the case of a solid, such as potassium chloride, under the above conditions. The density of potassium chloride is 1·99. If 2 grams of the salt are weighed, the apparent loss in weight (= weight of air displaced) is $2 \times 0{\cdot}0012/1{\cdot}99 = 0{\cdot}0012$ grams. The apparent loss in weight for the brass weights is $2 \times 0{\cdot}0012/8{\cdot}4 = 0{\cdot}00029$ grams. Hence 2 grams of potassium chloride will weigh $0{\cdot}0012 - 0{\cdot}00029 = 0{\cdot}00091$ grams less in air than " in vacuo," a difference of 0·05 per cent.

It must be pointed out that for most analytical purposes where it is desired to express the results in the form of a percentage, the ratio of the weights in air, so far as solids are concerned, will give a result which is practically the same as that which would be given by the weights " in vacuo." Hence no buoyancy correction is necessary in these cases. However, where absolute weights are required, as in the calibration of volumetric glassware, corrections for the buoyancy of the air must be made (compare Section **II, 20**).

Let us now consider the general case. It can be shown that if W_v = weight " in vacuo," W_a = apparent weight in air, d_a = density of air, d_w = density of the weights, and d_b = density of the body, then :

$$W_v = W_a + d_a\left(\frac{W_v}{d_b} - \frac{W_a}{d_w}\right) \qquad \text{(i).}$$

The density of the air will depend upon the humidity, the temperature and the pressure. For an average humidity (50 per cent) and average conditions of temperature and pressure in a laboratory, the density of the air will rarely fall outside the limits 0·0011 and 0·0013 g./ml. It is therefore permissible for analytical purposes to take the weight of 1 ml. of air as 0·0012 g.

Since the difference between W_v and W_a does not usually exceed 1 to 2 parts per thousand, we may write :

$$\begin{aligned} W_v &= W_a + d_a\left(\frac{W_a}{d_b} - \frac{W_a}{d_w}\right),\\ &= W_a + W_a\left\{0{\cdot}0012\left(\frac{1}{d_b} - \frac{1}{8{\cdot}4}\right)\right\} \quad \text{[for brass weights, } d_w = 8{\cdot}4\text{]}\\ &= W_a + kW_a/1000, \end{aligned}$$

$$\text{where} \quad k = 1{\cdot}20\left(\frac{1}{d_b} - \frac{1}{8{\cdot}4}\right).$$

The values of k for $d_a = 0{\cdot}0012$ and $d_w = 8{\cdot}4$ have been calculated and are collected in the following Table. If a substance of density d_b weights W_a grams in air, then $W_a.k$ *milligrams* are to be added to the weight in air in order to obtain the weight " in vacuo." The correction is positive if the substance has a density lower than that of brass and negative if the density of the substance is greater than that of brass.

TABLE XXIV. REDUCTIONS OF WEIGHINGS MADE IN AIR WITH BRASS WEIGHTS TO " VACUO."

d_b	k	d_b	k	d_b	k
0·5	+ 2·26	1·9	+ 0·49	11·0	− 0·03
0·6	+ 1·86	2·0	+ 0·46	12·0	− 0·04
0·7	+ 1·57	2·5	+ 0·34	13·0	− 0·05
0·8	+ 1·36	3·0	+ 0·26	14·0	− 0·06
0·9	+ 1·19	3·5	+ 0·20	15·0	− 0·06
1·0	+ 1·06	4·0	+ 0·16	16·0	− 0·07
1·1	+ 0·95	4·5	+ 0·13	17·0	− 0·07
1·2	+ 0·86	5·0	+ 0·10	18·0	− 0·08
1·3	+ 0·78	5·5	+ 0·08	19·0	− 0·08
1·4	+ 0·72	6·0	+ 0·06	20·0	− 0·08
1·5	+ 0·66	7·0	+ 0·03	21·0	− 0·09
1·6	+ 0·61	8·0	+ 0·01	22·0	− 0·09
1·7	+ 0·56	9·0	− 0·01	23·0	− 0·09
1·8	+ 0·52	10·0	− 0 02	24·0	− 0·09

II, 8. Calibration of weights.—All weights should be calibrated in order to detect any inaccuracies amongst the weights themselves. This calibration should be repeated at least once a year, because changes may occur owing to wear, corrosion or other causes. In all good sets of weights the duplicate and triplicate weights are distinguished by the marking of one * or two ** asterisks on the surface. If this is not the case, the set should either be returned to the makers or the markings made with a suitable punch by a qualified mechanic in the instrument workshop of the Institution.

The simplest and best method of calibration is to check each piece of a set against a corresponding piece of a set calibrated by a nationally recognised laboratory.* The method of substitution is employed. A third or subsidiary set of weights is also required. First, place the smallest weight of the set to be calibrated on the right-hand pan and balance it by the corresponding piece of the subsidiary box of weights placed on the left-hand pan. Ascertain the rest point by the method of swings. Remove the weight from the right-hand pan and replace it by a piece of the same denomination from the standard set of weights, and determine the rest point again. The error in the weight can then be computed from the difference in the rest point in the two weighings and the known sensitivity of the balance for the load in question. This process is repeated for every piece in the box of weights. Finally a table is constructed showing the absolute error for each weight.

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* For the British Empire, this is the National Physical Laboratory ; for U.S.A., the Bureau of Standards, etc.

Complete sets of standard weights are not always available. A modification of the method due to T. W. Richards (1900), which is essentially a calibration of the weights relative to one another, is then employed. Here also the substitution method of weighing is utilised ; an extra set of weights, to act as a tare, is also required. The principle of the method is to assume that the smallest weight in the set, say one of the 10 mg. pieces, is correct, and the value of every other weight in the set is obtained in terms of it. The weighings must be made by the method of swings. The values for the larger weights are found to differ considerably from the nominal values because such a small standard was used. It is therefore usual to change the relative standard to one of the larger weights, say, to a nominal 10 g. piece, and to express all the other pieces in terms of the larger standard. The differences will then be much smaller. If the absolute value of the new standard can be determined by comparison with a similar standard weight (calibrated by the N.P.L., Bureau of Standards, etc.), we can then readily calculate the absolute values of all the other weights, since the ratio of the 10 g. weight to all the others in the set has been determined.

The detailed procedure is as follows. The sensitivity of the balance at different loads must be known. If this is not the case, it must be determined as described in Section **II, 6A.** Leave the weights for at least 30 minutes before commencing the calibration. Place one of the 10 mg. weights, temporarily assumed as exactly 10 mg., on the right-hand scale pan, and counterpoise it with the corresponding weight from the subsidiary set on the left-hand pan. Determine the rest point by the method of swings ; this should be near the centre of the scale (division 10 in Fig. 2-2). Repeat the determination of the rest point for the other two 10 mg. weights (0·01* and 0·01**), retaining the original tare on the left-hand pan. Any difference in their weights can be calculated from the known sensitivity of the balance. Next place the two 0·01 g. pieces (say, 0·01 and 0·01*) on the right-hand pan, and counterbalance them with a 0·02 g. weight from the extra set. Determine the rest point. Repeat with the 0·02 g. weight from the set, using the same tare. The calibration correction for the 0·02 g. weight can then be determined, knowing that for the 0·01 g. and 0·01* g. Continue the comparison until the complete set is calibrated. The following comparisons will be made: 0·01* g. against 0·01 g., 0·01** g. against 0·01* g.; 0·02 g. against (0·01 + 0·01*) g.; 0·05 g. against (0·02, 0·01, 0·01*, 0·01**) g. = Σ 0·05; 0·1 g. against (0·05 + Σ 0·05) = Σ 0·1 g.; 0·1* g. against 0·1 g.; 0·2 g. against (0·1 + 0·1*) g.; 0·5 g. against (0·2 + 0·1 + 0·1* + Σ 0·1) g. = Σ 0·5; 1 g. against (0·5 + Σ 0·5) g.; 1* g. against 1 g.; 1** g. against 1* g.; 2 g. against (1 + 1*) g.; 5 g. against (2 + 1 + 1* + 1**) g.; 10 g. against (5 + 2 + 1 + 1* + 1**) g.; 10* g. against 10 g.; 20 g. against (10 + 10*) g.; 50 g. against (20 + 10 + 10* + 5 + 2 + 1 + 1* + 1**) g.

It is generally advisable to calibrate the rider also. Let us suppose this is of 10 mg. denomination. The rider is placed on position 10 of the beam and comparison is made directly with the 0·01 g., the assumed temporary standard placed on the left-hand pan. In some sets of weights there are only two 10 mg. pieces; in such cases the rider is kept at position 10 during the calibration.

The results should be tabulated as shown in Table XXV. This also illustrates the exact method of computation. The method of calculation of the relative values taking the 0·01 g. as correct is obvious. Column 7, the ideal calibration value, is most simply obtained by assuming that the 10 g. weight actually possesses the weight of 10·0385 g. (see Table) and taking this as the permanent standard; there is therefore no correction for this weight. The 5 g. pieces in this basis should weigh 5 × 10·0385/10 = 5·0193 g.; the other ideal calibration values are calculated in the same manner. The differences between columns 6 and 7 give the corrections to be added or subtracted to the nominal values of the weights. A table should be constructed showing the correction to be applied to each weight: the table may also contain the corrections for various combinations of weights.

TABLE XXV. CALIBRATION OF A SET OF ANALYTICAL WEIGHTS BY THE METHOD OF SUBSTITUTION.

Tare on left pan	*Nominal wt. on right pan*	*Rest point*	*Sensitivity div. mg.*	*Difference in g.*	*Relative values if 0·01 g. correct*	*Ideal calibration value*	*Correction in mg.*
0·01	0·01	10·4	5·0		0·0100	0·0100	0·0
	0·01*	10·4			0·0100	0·0100	0·0
	0·01**	10·4			0·0100	0·0100	0·0
0·02	0·01 + 0·01*	10·9			(0·0200)		
	0·02	9·9		+ 0·0002	0·0202	0·0201	+ 0·1
0·05	0·02, 0·01, 0·01*, 0·01**	10·7			(0·0502)		
	0·05	10·3		+ 0·0001	0·5003	0·0502	+ 0·1
0·1	0·05 + Σ0·05	10·6			(0·1003)		
	0·1	10·6		+ 0·0000	0·1003	0·1004	− 0·1
	0·1*	9·6		+ 0·0002	0·1005	0·1004	+ 0·1
0·2	0·1 + 0·1*	9·2			(0·2008)		
	0·2	10·7		− 0·0003	0·2005	0·2008	− 0·3
0·5	Σ 0·5	11·2			(0·5016)		
	0·5	10·3		+ 0·0002	0·5018	0·5019	− 0·1
1	0·5 + Σ0·5	11·3			(1·0034)		
	1	8·3		+ 0·0006	1·0040	1·0039	+ 0·1
	1*	9·3		+ 0·0004	1·0038	1·0039	− 0·1
	1**	10·3		+ 0·0002	1·0036	1·0039	− 0·3
2	1, 1*	10·4			(2·0078)		
	2	10·9		− 0·0001	2·0077	2·0077	0·0
5	2, 1, 1*, 1**	8·0			(5·0191)		
	5	9·2		− 0·0002	5·0189	5·0193	− 0·4
10	5, 2, 1, 1*, 1**	11·6	4·6		(10·0380)		
	10	9·3		+ 0·0005	*10·0385*	*10·0385*	± 0·0
	10*	11·6		0·0000	10·0380	10·0385	− 0·5
20	10, 10*	11·4	4·2		(20·0765)		
	20	11·4		0·0000	20·0765	20·0770	− 0·5
50	20, 10, 10*, 5, 2 1, 1*, 1**	12·0	3·6		(50·1910)		
	50	8·5		+ 0·0010	50·1920	50·1925	− 0·5

Attention is directed to the fact that for quantitative work we rarely require to know the absolute weight, since we are nearly always concerned with weight *ratios*. It is of the utmost importance that the weights should agree among themselves, *e.g.*, the 2 g. piece should be exactly twice the 1 g.

weight, etc. Except for the most expensive sets, we rarely find that these adjustments have been carried out with sufficient accuracy. Hence it is imperative that all sets of weights should be calibrated or standardised by one of the methods just outlined.

II, 9. Other types of balances.—The instrument described in Section **II, 2** is spoken of as an ordinary balance, and is the type that is most widely used for analytical work. In the last few decades a number of changes have been made in the design of balances, chiefly with the objects of rendering the operation of weighing more convenient and more rapid. Some of these will be mentioned below.

A. The chainomatic balance. This balance is similar to an ordinary chemical balance in general construction, but differs from it in that the use of fractional weights below 100 mg. and the rider are entirely eliminated. A rolled-gold or gold chain is attached to one end of the beam and at the other end to a small vernier movable along a vertical column, graduated in mms. and situated to the right of the balance beam. This sliding vernier or block is controlled by turning a handle or screw outside the balance case. It will be evident from Fig. 2–6* that the weight of the chain is carried both by the beam and the vernier block; the higher the latter, the smaller is the proportion of the weight carried by the beam. The column is graduated to read directly in mg. up to 100 mg., and with the aid of the vernier block readings can easily be

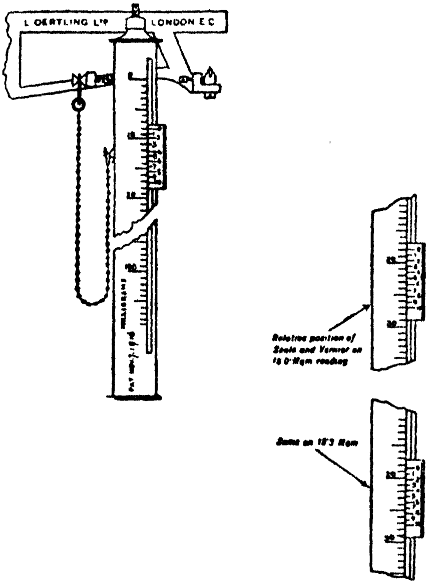

FIG. 2–6.

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* This Figure is reproduced by courtesy of L. Oertling, Ltd., 65 Holborn Viaduct, London, E.C.1, England.

made to 0·1 mg. (see Figure 2–6). In some types of chainomatic balances, the beam is serrated into 10 equal parts from " 0 " on the extreme left to " 10 " on the extreme right, and is adjusted with the aid of a special 5 decigram rider at zero, each serration or notch being equivalent to one decigram. In this type of balance the use of fractional weights is completely eliminated.

The chief advantages of chainomatic balances are: (i) Weights less than one decigram (in some balances one gram) are unnecessary. (ii) The frequent opening and closing of the balance case towards the end of a weighing are avoided; the chainomatic mechanism can be operated whilst the balance is swinging. (iii) The weighings can be carried out rapidly.

B. The air damped balance. An oscillating system, such as a balance, is said to be damped if it is subject to some force which restrains its motion and decreases the amplitude of its swings. All balances are damped to a slight extent since friction cannot be entirely eliminated. In the air damped balance, large light pistons attached to the pans or to the beam move loosely in large cylinders. The resultant damping is so great that the pointer swings slowly from the centre to the rest point within 10 to 15 seconds. The sensitivity of the balance is not decreased by damping. In weighing it is therefore only necessary to note the point of rest. Some balances (*e.g.*, those of Bunge) have a scale which is graduated to correspond to milligrams and the rest point is observed through a microscope. In other balances (*e.g.*, those of Oertling) a finely-divided graticule is attached to the end of the pointer and an enlarged reflection of the scale is projected on to an illuminated ground-glass screen situated in a convenient position at the top of the balance case. The graticule is divided into 500 equal parts, and balances are available in which the 500 divisions correspond to either 0·05 gram or 0·5 gram; in the former case weights below 0·05 gram are unnecessary, and in the latter case all fractional weights are eliminated.

C. The magnetically damped balance. Damping can also be effected by suitably suspending a small aluminium plate from the right-hand stirrup of the balance; a counterpoise, usually of brass, is suspended from the left-hand stirrup. The aluminium plate moves between, but does not quite touch, the poles of a powerful permanent horse-shoe magnet, which is attached rigidly to a support, which may be mounted on the central pillar or independently. The effect is very similar to the air damped balance. It has been stated that ferrous materials can be weighed on this balance without appreciable error.

GENERAL APPARATUS, REAGENTS AND OPERATIONS

In the following pages an account will be given of the general apparatus and reagents of quantitative analysis. Apparatus which is confined either to volumetric or gravimetric analysis will be described in the Sections devoted to these.

II, 10. General apparatus.—A. Burners. The ordinary **Bunsen burner** is widely employed for the attainment of moderately high temperatures. It is important that the air regulator should be in working order. The maximum temperature is attained by adjusting the regulator so as to admit rather more air than is required to produce a non-luminous flame ; too much air gives a noisy flame, which is unsuitable.

An improvement in the design has been effected in burners in which both the gas and air supply can be regulated. The flow of gas is controlled at the base of the burner by means of a screw which operates a needle valve ; the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more or less air to enter through the holes at the base. The **Pittsburgh universal burner*** (sometimes termed a **Tirril burner**) and one of the Fletcher burners† are of this type. It is claimed that a temperature of 1050–1100°C can be produced in a covered platinum crucible with these burners.

With a **Méker burner** a temperature of 1200°C is said to be reached in a covered platinum crucible. The volume of air passing through a fully aerated ordinary Bunsen burner is about 2·5 times the volume of the gas ; for the complete combustion of coal gas about 6 volumes of air are necessary. If a mixture of coal gas and air in the latter proportions were lighted at an ordinary Bunsen burner, the flame would " strike back " and burn at the bottom of the tube. In the Méker burner (Fig. 2–7, *a*) the holes for the admission of air are large enough to pass sufficient air for the complete combustion of the gas, and the tube is narrowest near the base and widens out near the top, thus resulting in a more perfect mixing of the gas with air ; a nickel grid is fitted into the top of the burner in order to prevent the flame striking back. The gas burns in many small flames with the top of each inner reducing cone about 1 mm. above the top of the burner. The numerous small flames combine to give a very hot and highly concentrated flame, which is oxidising in character except below the tips of the tiny flames ; the maximum temperature is attained just a little above the small flames, *i.e.*, about 2 to 3 mm. from the top of the burner. The burner is used for the ignition of precipitates that require a high temperature for conversion into a weighable form, and also for some fusions. A blow-pipe flame or " blast lamp " is sometimes used for these purposes, but in most cases equally satisfactory results are obtained with the Méker burner. An improved form of the ordinary Méker burner (*e.g.*, in the **Fisher "high temperature" burner** Fig. 2–7, *b*) contains an arrangement for adjusting both the gas and air supplies as in the Pittsburgh universal burner already described.

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* Manufactured by the Fisher Scientific Company, 711–723 Forbes Street, Pittsburgh, Pa., U.S.A.

† Manufactured by Fletcher, Russell and Co. Ltd., Palatine Works, Warrington, England.

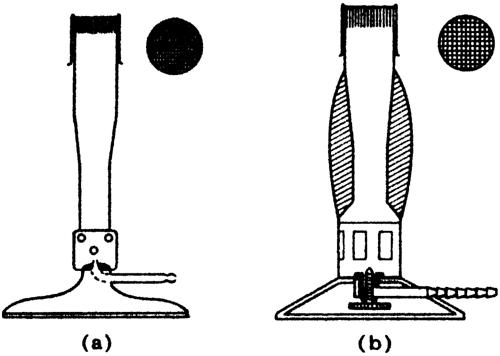
(a) (b)

FIG. 2–7.

The **"Amal" burner*** attempts to combine the chief features of the improved Bunsen burner and the Méker burner. The flame can be turned down very low without flashing back, and it also furnishes a very hot flame. This is a very useful burner, but is comparatively expensive.

B. Wash bottles. A wash bottle is a flat-bottomed flask fitted up to deliver a fine stream of distilled water or other liquid for use in the transfer and washing of precipitates. A convenient size is a 500 to 750 ml. flask of Pyrex or other resistance glass ; it should be fitted up as shown in Fig. 2–8. A rubber bung is used, and the glass tubes above the bung should be in the same straight line and lie in the same plane. The jet should deliver a fine stream of water ; a suitable diameter of the orifice is 1 mm. All glass tubing must be rounded in the Bunsen flame after cutting.

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* Manufactured by Amal Ltd., Holford Works, Perry Bar, Birmingham, England.

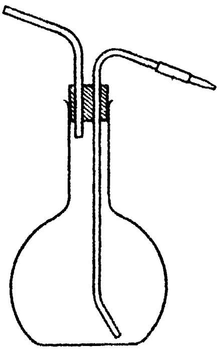

FIG. 2–8.

Thick string, thin sheet cork or other insulating material, held in place by copper wire, should be wrapped round the neck of the flask in order to protect the hand when hot water is used. In order to protect the mouth from scalding by the back rush of steam through the mouth piece when the blowing is stopped, it is convenient to use a three-holed rubber stopper and a short piece of glass tubing open at both ends is inserted in the third hole. The thumb is kept over this tube whilst the water is being blown out, and is removed immediately before the mouth pressure is released.

All-glass wash bottles, fitted with ground-glass joints, can be purchased. They should be used with organic solvents that attack rubber.

C. Distilled water. Distilled water must be employed in all analytical work. Various forms of still are in common use. It is important that the vessel containing the boiling water, which may be of almost any material, should be so separated from the condenser that there is little or no danger of spray entering the latter. The condenser should be of pure tin or, if this is not possible, be heavily plated with tin. The distilled water thus prepared may contain small quantities of dissolved ammonia and carbon dioxide. For water analysis and other purposes requiring highly purified water, the distilled water should be re-distilled from alkaline potassium permanganate, and the head and tail fractions rejected ; most of the dissolved ammonia is removed by this process. The most convenient method for the preparation of highly purified water (the so-called conductivity water) is to employ a special type of still, such as that designed by the writer* ; in this the steam is fractionally condensed and two grades of conductivity water are simultaneously produced.

* Obtainable from Baird and Tatlock (London) Ltd., 16–17 Cross Street, London, E.C.1, England.

D. Glassware. In order to avoid the introduction of impurities during analysis, resistance glass apparatus should be employed. For most purposes Pyrex glass (a boro-silicate glass) is to be preferred ; with strongly alkaline solutions, however, the author finds Jena glass to be more resistant. For elementary work, Chance's glass or Chance's " Hysil " glass, which is cheaper, is quite satisfactory. As a rule glassware should not be heated with a naked flame ; they should be heated on a wire gauze, preferably with an asbestos centre.

The most satisfactory **beakers** for general use are those provided with a spout. The advantages of this form are : (*a*) convenience of pouring, (*b*) the spout forms a convenient place at which a stirring rod may protrude from a covered beaker, and (*c*) the spout forms an outlet for steam or escaping gas when the beaker is covered with an ordinary clock glass. The size of a beaker must be selected with due regard to the volume of the liquid which it is to contain. The most useful sizes are from 250 to 600 ml. For evaporations with high boiling point liquids, *e.g.*, sulphuric acid, the shallow squat type of beaker is preferable.

Conical (or Erlenmeyer's) **flasks** of 200 to 500 ml. capacity find many applications, for example, in titrations.

Funnels should enclose an angle of 60°. The most useful sizes for quantitative analysis are those with diameters of 5·5, 7 and 9 cms. The stem should have an internal diameter of about 4 mm. and should be not more than 15 cms. long. For filling burettes and transferring solids to graduated flasks, a short stem, wide-necked funnel is useful.

E. Porcelain apparatus. Porcelain is generally employed for operations in which hot liquids are to remain in contact with the vessel for prolonged periods. It is usually considered to be more resistant to solutions, particularly alkaline solutions, than glass, although this will depend primarily upon the quality of the glaze. Shallow porcelain basins with lips are employed for evaporations. **Casseroles** are lipped, flat-bottomed porcelain dishes provided with handles ; they are more convenient to use than dishes.

Porcelain **crucibles** are very frequently utilised for igniting precipitates and heating small quantities of solids because of their cheapness and their ability to withstand high temperatures without appreciable change. Some reactions, such as fusion with sodium carbonate or other alkaline substances, and also evaporations with hydrofluoric acid cannot be carried out in porcelain crucibles owing to the resultant chemical attack. A slight attack of the porcelain also takes place with pyrosulphate fusions.

F. Fused silica apparatus. Two varieties of silica apparatus are available commercially, the translucent and the transparent grades. The former is much cheaper and can usually be employed instead of the transparent variety. The advantages of silica ware are : (*a*) its great resistance to heat shock because of its very small coefficient of expansion, (*b*) it is not attacked by acids at a high temperature except by hydrofluoric acid and phosphoric acid and, (*c*) it is more resistant to pyrosulphate fusions than is porcelain. The chief disadvantages of silica are : (*a*) it is attacked by alkaline solutions and particularly by fused alkalis and carbonates, (*b*) it is more brittle than ordinary glass, and (*c*) it requires a much longer time for heating and cooling than does, say, platinum apparatus.

G. Platinum apparatus. This is discussed fully in Section **II, 37.** Mention may, however, be made here of the resistance of platinum ware to fusions with sodium and/or potassium carbonate, and to evaporations with hydrofluoric acid and other single acids. A great advantage is its high thermal conductivity : a red hot platinum crucible placed in a desiccator to cool is ready for weighing after about 25 minutes.

H. Silver apparatus. The chief uses of silver crucibles and dishes in the laboratory are in the evaporation of alkaline solutions and for fusions with caustic alkalis ; in the latter case, the silver is slightly attacked. Silver melts at 960° and care should therefore be taken when heated over a bare flame.

I. Nickel ware. Crucibles and dishes of nickel are employed for fusions with alkalis and with sodium peroxide. In the peroxide fusion a little nickel is introduced, but this is usually not objectionable. No metal entirely withstands the action of fused sodium peroxide. Nickel oxidises in air, hence nickel apparatus cannot be used for operations involving weighing.

J. Iron ware. Iron crucibles may be substituted for those of nickel in sodium peroxide fusions.. They are not so durable, but are much cheaper.

K. Bakelite apparatus. This synthetic resin is unaffected by hydrofluoric acid at the ordinary temperature. Bakelite funnels, measuring cylinders, etc., are available for use with this acid.

L. Stirring rods. These are made from glass rod 3 to 5 mm. in diameter, cut into suitable lengths. Both ends should be rounded by heating in the Bunsen or blowpipe flame. The length of the stirring rod should be suitable for the size and the shape of the vessel for which it is employed, *e.g.*, for use with a beaker provided with a spout, it should project 3 to 5 cm. beyond the lip when in a resting position.

A stirring rod of convenient size should be provided with a short piece of rubber tubing fitted tightly over one end. This is the so-called **policeman** ; it is used for detaching particles of a precipitate adhering to the side of a vessel which cannot be removed by a stream of water from a wash bottle ; it should not, as a rule, be employed for stirring nor should it be allowed to remain in a solution.

M. Boiling rods. Boiling liquids and liquids in which a gas, such as hydrogen sulphide, sulphur dioxide, etc., has to be removed by boiling can be prevented from superheating and "bumping" by the use of a boiling rod (Fig. 2–9). This consists of a piece of glass tubing closed at one end and sealed approximately 1 cm. from the other end ; the latter end is immersed in the liquid. When the rod is removed, the liquid in the open end must be shaken out and the rod rinsed with a jet of water from a wash bottle. This device should not be used in solutions which contain a precipitate.

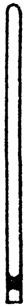

Fig. 2–9.

N. Desiccators. An ordinary Scheibler-type of desiccator (Fig. 2–10, *A*) is used for maintaining a dry atmosphere in which to place objects that

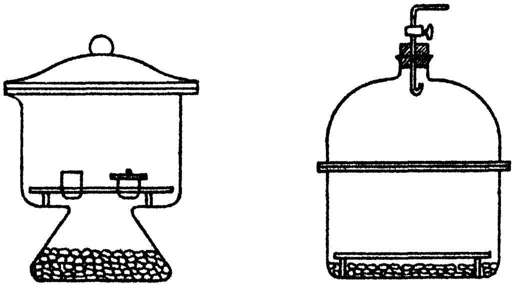

Fig. 2–10.

might be affected by moisture or carbon dioxide. The drying agent (usually calcium chloride in elementary work) is placed in the lower compartment, and the upper compartment is fitted up for the accommodation of crucibles, weighing bottles, etc. For small desiccators, a silica triangle with wire ends is bent so that the ends are perpendicular to the plane of the triangle, and then the wire ends spread out sufficiently so that they press against the walls and floor of the compartment and thus held firmly into position. With large desiccators, a porcelain plate on feet (Fig. 2–10, *A*), provided with apertures for crucibles, etc., is to be preferred : it should be wedged into the sides, if necessary, with cork or some other material. The ground edge of the desiccator should be lightly coated with white vaseline or a special grease in order to make it air tight ; too much grease may permit the lid to slide.

When a hot object is placed in a desiccator, about 5 to 10 seconds should elapse for the air to become heated and expanded before putting the cover in place. In removing the object, the cover should be slid open very gradually in order to prevent any sudden inrush of air due to the partial vacuum which exists owing to the cooling of the expanded gas content of the desiccator and to desiccation and thus prevent the precipitate being blown out of the crucible.

A desiccator is also employed for thorough drying of solids for analysis and other purposes. A very convenient type is portrayed in Fig. 2–10, *B*, a form of " vacuum " desiccator ; these are made of thick glass and should be tested by the manufacturers for use with a high vacuum. Large surfaces of the solid can be exposed, and the whole can be evacuated ; drying is thus much more rapid than in the ordinary Scheibler desiccator.

The most commonly used desiccant is granular, fused calcium chloride ; the 3–8 mesh size is very suitable, but the fused lumps are often employed on account of cheapness. In point of fact the so-called anhydrous calcium chloride (the hydrated crystalline variety is useless for this purpose) is not a very efficient drying agent (it usually contains about 1/4 molecule of water), but it is satisfactory for most purposes. Phosphorus pentoxide is the most powerful common desiccant known ; it should be used only when it is absolutely necessary, and must be renewed as soon as a crust forms over its surface. Concentrated sulphuric acid is better than calcium chloride ; it should be poured over pumice or broken glass, and must be replaced as soon as it shows signs of darkening. Resublimed iodine must not be dried over sulphuric acid. Silica gel, which has been dried at 130°C and allowed to cool over phosphoric oxide, contains about 11 per cent of water and is an extremely useful desiccating agent. In recent years two new desiccants have found wide application, *viz.*, magnesium perchlorate trihydrate (" dehydrite ") and anhydrous magnesium perchlorate (" anhydrone "). They are comparatively expensive for use in desiccators; anhydrone is, however, extensively employed in the quantitative absorption of water. Anhydrone rivals phosphorus pentoxide in its power of desiccation ; it can absorb about 50 per cent of its weight of water, and can be regenerated by suitable means. The following Table, due largely to J. H. Bower (1934), contains results which indicate the comparative drying powers of a number of desiccants.

TABLE XXVI. COMPARATIVE EFFICIENCY OF VARIOUS DRYING AGENTS.

Material	*Residual water per litre of air in mg.*	*Material*	*Residual water per litre of air in mg.*
$CuSO_4$ (anhyd.)	2·8	Silica gel	0·03
$CaCl_2$ (gran. anhyd., tech.)	1·25–1·5	KOH (sticks)	0·014
		Al_2O_3	0·005
$ZnCl_2$ (sticks)	0·98	$CaSO_4$ (anhyd.)	0·005
$Ba(ClO_4)_2$ (anhyd.)	0·82	CaO	0·003
NaOH (sticks)	0·80	$Mg(ClO_4)_2$ (anhyd.)	0·002
$CaCl_2$ (pure, anhyd.)	0·36	BaO	0·0007
$Mg(ClO_4)_2, 3H_2O$	0·03	P_2O_5	0·00003

It is evident from this Table that a hygroscopic material such as ignited alumina or lime should not be cooled over calcium chloride ; either anhydrone or phosphoric oxide is suitable.

Attention is directed to an all-aluminium desiccator (the Fisher " desicooler ") which is now marketed.* It is fitted with a shelf containing three holes to accommodate three sizes of crucible, and employs activated alumina as the desiccant (corrosion of the aluminium may occur with other desiccants). The charge of about 60 g. of activated alumina may be reactivated when exhausted by simply heating to 175°C. This desiccator should prove useful for general students' use since it is unbreakable and inexpensive.

* Obtainable from the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.

O. Test papers. With the development of more refined methods of quantitative analysis, the use of litmus paper as a rough indicator for determining the acidity and alkalinity of solutions has become obsolete. Paper strips coated with indicators are now available commercially* in books or in cork-stoppered glass vials. These include the following (the *p*H ranges are given between the parentheses): thymol blue (1·2 to 2·8); bromo-phenol blue (2·8 to 4·6); congo red (3·0 to 5·0); methyl red (4·2 to 6·3); propyl red (4·6 to 6·6); bromo-cresol purple (5·2 to 6·8); bromo-thymol blue (6·0 to 7·6); phenol red (6·8 to 8·4); cresol red (7·2 to 8·8); and ortho-cresolphthalein (8·2 to 9·8).

The most outstanding advance, however, is the Fisher alkacid" paper,† which will indicate the approximate hydrogen ion concentration over the *p*H range 2 to 10 to about ± 1 *p*H unit. Thus such terms as strongly acid, weakly acid, strongly alkaline or weakly alkaline assume a real significance with this test paper. When an "alkacid" test paper is immersed in a solution, it assumes the following colours: red at *p*H 2, orange at *p*H 4, yellow at *p*H 6, green at *p*H 8, and blue at *p*H 10. Each vial of test papers contains a 5-colour chart printed on the label, which facilitates matching.

P. Centrifuge. A small electrically-driven centrifuge is a useful apparatus for an analytical laboratory. It may be employed for removing the mother liquor from recrystallised salts, for collecting difficultly filterable precipitates, and for the washing of certain precipitates by decantation.

II, 11. Reagents.—The purest available reagents, both liquid and solid, should be used for quantitative analysis. The analytical reagent quality is generally employed. Most manufacturers now state the various percentages of impurities on the label, and some give a guarantee that certain impurities do not exceed certain definite limits.‡ It must be remembered that the label is not an infallible criterion for the following reasons:

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* These may be obtained, for example, from E. H. Sargent and Co., Chicago, U.S.A., or from Hopkin and Williams Ltd., London, E.C.2, England.

† Supplied by the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.

‡ See *Analar Standards for Laboratory Chemicals*, Second Edition, 1937, published jointly by Hopkin and Williams Ltd., 16–17 Cross Street, London, E.C.1, and by British Drug Houses Ltd., Graham Street, London, N.1, England. See also the Analytical Reagents Catalogues of the Mallinckrodt Chemical Works, of 72–74 Gold Street, New York, N.Y., U.S.A., of the J. T. Baker Chemical Co. Phillipsburg, N.J., U.S.A., of Baker and Adamson, 40 Rector Street, New York, U.S.A., and of The Coleman and Bell Co., Norwood, Ohio, U.S.A. These American firms, particularly the first-named, have a very wide range of analytical reagents and many conform with the specifications for analytical reagents issued by the American Chemical Society (see Appendix Section **A, 9**).

(i) Some impurities may not have been tested for by the manufacturer.

(ii) In spite of the greatest care exercised in packing, foreign materials, such as dust, small pieces of cork, paper, etc., may be accidentally introduced.

(iii) The reagent may have been contaminated after its receipt from the manufacturers either by the stopper having been left open for some time with the consequent exposure of the contents to the laboratory atmosphere or by the innocent return of an unused portion of the reagent to the bottle.

(iv) In the case of a solid reagent, it may not be sufficiently dry. This may be due either to insufficient drying by the manufacturers or to leakage through the stoppers during storage, or to both of these causes.

However, if the analytical reagents be purchased from a manufacturing firm of repute, and instructions given (*a*) that no bottle is to be opened for a longer time than is absolutely necessary, and (*b*) that no reagent is to be returned to the bottle after it has been removed, the likelihood of any errors arising from some of the above possible causes is considerably reduced. The exact mode of drying, if necessary, will vary with the reagent; details are given in the text in connexion with their use. In all cases of doubt as to the purity of the reagents used, they should be tested by standard methods* for the impurities that might cause errors in the determinations. It must be mentioned that not all chemicals employed in quantitative analysis are available in the form of analytical reagents; the purest commercially available products must then be purified by known methods, some of which are given below.

For expressing concentrations of reagents, the molar system is universally applicable, *i.e.*, the number or fraction of gram molecular weights present in 1 litre of solution. Concentrations may also be expressed in terms of normality if no ambiguity is likely to arise (compare Section **I, 23**). All reagent bottles should be kept scrupulously clean, particularly round the neck and mouth. The stopper should never be laid on the bench, but should be held between the fingers or placed upon a clean watch glass; it should be returned immediately to its bottle as soon as the reagent has been removed.

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* See, for example, J. Rosin, *Reagent Chemicals and Standards*, 1937 (Chapman and Hall).

II, 12. Purification of substances.—Space does not permit more than a short discussion of a few of the most important methods of purification which are likely to be employed by the student.

A. Recrystallisation of solids. This is the commonest method of purification ; the usual solvent is water. A known weight of the solid is dissolved in a volume of water sufficient to give a saturated or nearly saturated solution at the boiling point : a beaker, conical flask or porcelain dish may be used. The hot solution is filtered through a fluted filter paper placed in a funnel with a short stem, and the filtrate collected in a beaker : this process will remove insoluble material which is usually present. If the substance crystallises out in the funnel, it should be filtered through a hot water funnel. In the latter, the conical portion of the funnel is surrounded by a double-walled copper vessel containing water, which can be heated either by placing a Bunsen burner beneath a hollow projection in direct communication with the copper jacket or, better, electrically. The clear hot filtrate is cooled rapidly by immersion in a dish of cold water or in a mixture of ice and water, according to the solubility of the solid ; the solution is constantly stirred in order to promote the formation of small crystals, which include less mother liquor and are therefore more pure than larger crystals. The solid is then separated from the mother liquor by filtration. The various funnels which may be employed for this purpose are shown diagrammatically in Fig. 2–11. (*a*) is the ordinary porcelain Buchner funnel ; (*b*) is the Jena Buchner " slit sieve " glass funnel. In both cases, one

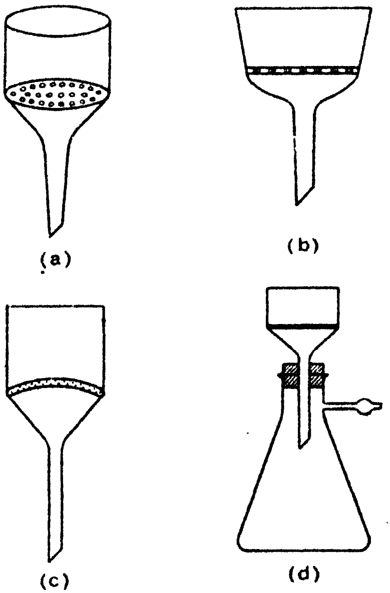

FIG. 2–11.

or, better, two good quality filter papers are placed on the plate; the Jena type is preferable since it is transparent and it is easy to see whether the funnel is perfectly clean. (*c*) is a Jena Buchner funnel with a sintered glass plate; no filter paper is required; strongly alkaline and acidic solutions can be readily filtered with this funnel. In all cases the funnel of appropriate size is fitted into a filter flask (*d*), and the filtration conducted under the diminished pressure provided by a filter pump or vacuum line. The solid may be pressed down on the funnel with a wide glass stopper, sucked as dry as possible, and then washed with small portions of the original solvent to remove the adhering mother liquor. The recrystallised solid is dried upon clock glasses at or above the laboratory temperature according to the nature of the material; care must of course be taken to exclude dust. Various methods for drying at temperatures above that of the room are described below. The dried solid is preserved in glass-stoppered bottles. It should be noted that unless great care is taken there is a danger of introducing a little filter paper with funnels (*a*) and (*b*), and small particles of glass with funnel (*c*) when the solid is removed.

Some solids are either too soluble, or the solubility does not vary sufficiently with temperature, in a given solvent for direct crystallisation to be practicable. In many cases, the solid can be precipitated from, say, a concentrated aqueous solution by the addition of a liquid, miscible with water, in which it is less soluble. Alcohol, in which most inorganic compounds are almost insoluble, is generally used. Care must be taken that the amount of alcohol or other solvent added is not so large that the impurities are also precipitated. Potassium bicarbonate and tartar emetic (potassium antimonyl tartrate) may be purified by this method.

B. Sublimation. This process is employed to separate volatile substances from non-volatile impurities. Iodine, arsenious oxide and ammonium chloride can be purified in this way. The substance is placed in a porcelain dish or casserole; the latter is gently heated with a small flame and the vapour condensed upon a cool surface, such as a large inverted glass funnel containing a plug of glass wool at the apex, or, preferably, a flask containing cold water.

Pure iodine is required in volumetric analysis, and details for its purification will not be out of place here. Grind together 10 g. of iodine with 4 g. of potassium iodide (the latter to retain any chlorine or bromine present as the non-volatile potassium salts) and transfer the mixture to a casserole: place a flask almost filled with cold water on the casserole *a* in Fig. 2–12. Heat very gently until sufficient iodine has sublimed on to the bottom of the flask, allow to cool, and remove the flask with the iodine adhering to it. Pass a rapid stream of cold water through the flask; this will cause the glass to contract somewhat and the whole of the crust can then be removed by scraping with a clean glass rod and is collected on a clock glass. Break up the large pieces, and repeat the sublimation without the addition of potassium iodide. Remove the second sublimate as before, and grind the iodine in a glass mortar. Dry in a desiccator containing calcium chloride; no grease whatever should be exposed on the inside, since iodine vapour attacks grease forming hydrogen iodide.

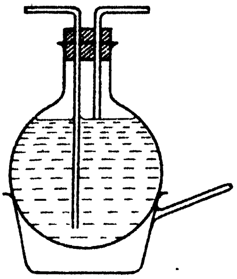

FIG. 2–12.

II, 13. Heating apparatus.—A. Steam baths. These are used for the slow evaporation of liquids, digestion of precipitates, etc. The simplest form is a lipped beaker in which water is boiled, the vessel being supported on the rim. Generally, a copper vessel, about half-filled with water and heated by a Bunsen burner, is employed. The upper portion is fitted with a series of flat, sheet copper rings of gradually diminishing diameter so that vessels of various sizes can be accommodated. If the water bath is a large one, the upper portion is fitted with a cover containing holes of various sizes, and each aperture may be provided with its own series of concentric rings or with an individual cover: vessels of various dimensions can thus be heated at the same time. It is advantageous to fit a constant-level device to the water bath; the danger of running dry and consequent overheating is thus eliminated. In some laboratories, the water bath may be connected to a direct steam supply.

B. Steam ovens. A steam oven is usually made of copper and, with the exception of the door, is double-cased throughout. The casing is filled to about one fourth of its height with water and is heated by means of a Bunsen or other burner. The water is kept boiling gently and the steam is condensed by a suitable condenser and returned as water to the oven.

In many laboratories the heating of steam ovens is carried out simultaneously with the distillation of water in the so-called combined steam oven and still. The temperature inside a steam oven usually does not exceed 90° to 95°C.

C. Electric ovens. The most convenient type is an electrically heated, thermostatically controlled drying oven having a temperature range from room temperature to about 250°–300°C. These are comparatively inexpensive and should form part of the normal equipment of every analytical laboratory. The temperature can be controlled to within ± 1–2°C. They are used principally for drying precipitates or solids at comparatively low controlled temperatures.

D. Muffle furnaces. An electrically heated furnace of muffle form should be available in every well-equipped laboratory. The maximum temperature should be about 1200°C. If possible, a thermo-couple and indicating pyrometer should be provided ; otherwise the ammeter in the circuit should be calibrated, and a chart constructed showing ammeter and corresponding temperature readings. Gas heated muffles may also be used, but are not so convenient in practice ; the maximum temperature is about 1000°C.

E. Hot plates. The electrically-heated hot plate, preferably provided with three controls, " Low," " Medium " and "High," is almost indispensable for analytical laboratories. The heating elements and the internal wiring should be totally enclosed ; this protects them from fumes and spilled liquids. The three-heat rectangular type is particularly suitable where a number of evaporations are to be carried out simultaneously.

F. Air baths. For drying solids and precipitates at temperatures up to 250°C in which acid or other corrosive vapours are evolved, an electric oven should not be used. An air bath may be constructed from a circular metal (copper, iron, or nickel) vessel, lined round the sides and at the bottom with two thicknesses, 1/8" thick, of asbestos board ; it is advisable to soak the asbestos in water before placing it in position. The cover consists of an asbestos board, 1/4" thick, provided with a hole for the insertion of a thermometer supported upon a cork. A silica triangle, the legs of which are appropriately bent, is inserted inside the bath for supporting a clock glass, etc. The whole is heated by a Bunsen flame, which is shielded from draughts ; the temperature can be readily maintained constant with 2 to 3°C. Recently, an air bath of similar construction, but with special Jena glass sides (Fig. 2–13) has been introduced ; this possesses the obvious advantage of visibility inside the air bath.

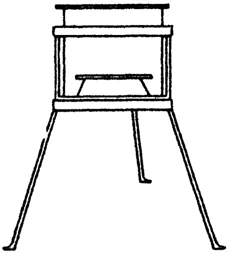

FIG. 2–13.

A form of air bath, which is very useful for the speedy evaporation of liquids (including concentrated sulphuric acid) at almost any temperature and also for the dehydration of many solids, is known as a **radiator.** It is constructed of sheet iron or nickel bent into the form of a cone (Fig. 2–14, *A*) ; the bottom *B*, also of nickel or iron, but best of platinum, is fixed to the cone by bending the notched edges over one another. A convenient size is 7 cm. high, 7 cm. wide at the top and 5 cm. at the bottom. A triangle of silica, porcelain or platinum is suspended inside the radiator either by cutting three narrow slits to a suitable depth and placing the wire ends of the triangle through these (as in Fig. 2–14, *C*) or the wire ends may be bent over the upper rim of the cone.* The crucible or dish is supported on the triangle. The radiator is mounted on a tripod and heated directly by a burner ; alternatively, it may be heated on a hot plate. Evaporations may thus be carried out speedily without bumping. When very rapid evaporation is required, a metal ring with an opening somewhat larger than the mouth of the crucible, etc., is placed upon the top of the radiator.

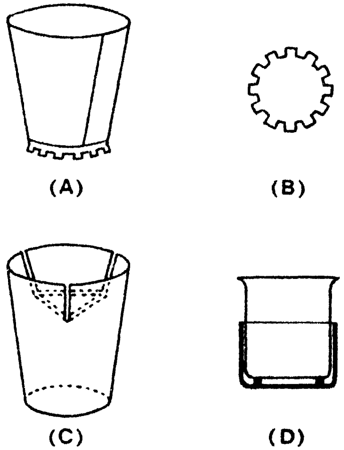

FIG. 2–14.

Another device of similar character is due to J. J. Moroney. It consists of a metal cylinder, which is usually made of a cast-aluminium alloy ; the inside bottom is provided with three small projections upon which the beaker rests. There is only a small clearance around the beaker and the evaporator (Fig. 2–14, *D*). The beaker is thus heated on the sides as well as the bottom, and has three small hot spots on the bottom at which points the bubbles form when boiling takes place. The general superheating of the bottom is thus eliminated, together with the attendant "bumping." The Moroney evaporator is available commercially*; it eliminates the bumping experienced in evaporating heavy solutions, or hydroxides, sulphuric acid, and solutions containing a precipitate.

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* The apparatus, known as the Hillebrand-Willard crucible radiator, is commercially available. It is constructed from one piece of monel metal, and is marketed by the Central Scientific Co., 1700 Irving Park Blvd., Chicago, Ill., U.S.A.

II, 14. Sampling of solids.—Sampling is the process of extracting from a large quantity of material a small portion which is truly representative of the composition of the whole material. This process is of great importance since, if it is not satisfactorily done, the labour and time spent in making a careful analysis of the sample may be completely wasted. If the material is more or less homogeneous, sampling is comparatively simple. If, however, the material is bulky and heterogeneous, sampling must be carried out with great care, and the method will vary somewhat with the nature of the bulk solid. A detailed discussion of the methods of sampling is outside the scope of this book.†

The underlying principle for the sampling of material in bulk, say, of a truck load of coal or iron ore, is to select a large number of portions in a systematic manner from different parts of the bulk and then to combine them. This large sample of the total weight is crushed mechanically, if necessary, and then shovelled into a conical pile. Every shovelful must fall upon the apex of the cone and the shoveler must walk around the cone as he shovels ; this ensures a comparatively even distribution. The top of the cone is then flattened out and divided into quarters. Opposite quarters of the pile are then removed, mixed to form a smaller conical pile, and again quartered. This process is repeated, further crushing being carried out if necessary, until a sample of suitable weight (say, 200 to 300 g.) is obtained.

If the quantity of material is of the order of 2 to 3 kilos or less, intermixing may be accomplished by the method known as "tabling." The finely divided material is spread on the centre of a large sheet of oil-cloth or similar material. Each corner is pulled in succession over its diagonal partner, the lifting being reduced to a minimum; the particles are thus caused to roll over and over on themselves, and the lower portions are constantly brought to the top of the mass and thorough intermixing ensues. The sample may then be rolled to the centre of the cloth, spread out, and quartered as before. The process is repeated until a sufficiently small sample is obtained. The final sample for the laboratory, which is usually between 25 and 200 grams in weight, is placed in an air-tight bottle.

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* Obtainable from the Fisher Scientific Company, Pittsburgh, U.S.A.

† Readers are referred to the various publications of the British Standards Institution, *e.g.*, the British Standards Specifications, No. 403 for 1930, which contains a report on the sampling of small fuel, and incidentally discusses some general principles of sampling ; also to the references in Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929, p. 47, and in W. W. Scott-N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. II, p. 5, 1301 (5th edition, 1939).

The sampling of metals and alloys is best effected by drilling holes, preferably right through the central portion, of a representative test piece; *all* the material from the hole must be analysed as the fine dust may differ in composition from the more ductile drillings.

Before analysis the representative sample is usually dried at 105–110°C, or at some higher specified temperature if necessary, to constant weight. The results of the analysis are then reported on the "dry" basis, *viz.*, on a material dried at a specified temperature. The loss in weight on drying may be determined, and the results may be reported, if desired, on the original "moist" basis; these figures will only possess real significance if the material is not appreciably hygroscopic and no chemical changes, other than the loss of water, take place on drying.

In a course of systematic quantitative analysis, such as that with which we are chiefly concerned in the present book, the unknowns supplied for analysis are usually portions of carefully analysed samples which have been finely ground until uniform.

II, 15. Crushing and grinding.—If the material is hard (*e.g.*, a sample of rock), it is first broken into small pieces on a hard steel plate with a hardened hammer. The loss of fragments is prevented by covering the plate with a steel ring, or in some other manner. The small lumps may be broken in a "**percussion**" **mortar** (Fig. 2-15). The mortar and pestle are constructed entirely of hard steel. One or two small pieces are placed in the mortar, and the pestle inserted into position;

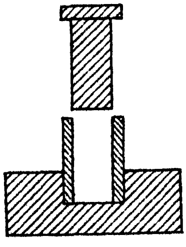

FIG. 2-15.

reagent. The most commonly used fusion reagents, or **fluxes** as they are called, are anhydrous sodium carbonate either alone or, less frequently, mixed with potassium nitrate or sodium peroxide, potassium or sodium pyrosulphate, sodium peroxide, sodium or potassium hydroxide. The flux employed will depend upon the nature of the insoluble substance. The vessel in which fusion is effected must be carefully chosen ; platinum crucibles are employed for sodium carbonate and potassium pyrosulphate ; nickel or silver crucibles for sodium or potassium hydroxide ; nickel, silver or iron crucibles for sodium carbonate and / or sodium peroxide ; nickel crucibles for sodium carbonate and potassium nitrate (platinum is slightly attacked). To carry out the fusion, a layer of the flux is placed at the bottom of the crucible, and then the intimate mixture of the flux and the finely-divided substance added ; the crucible should be about half-full, and should, generally, be kept covered during the whole process. The crucible is very gradually heated at first, and the temperature slowly raised to the required temperature. The final temperature should not be higher than is actually necessary ; any possible further attack of the flux upon the crucible is thus avoided. When the fusion, which usually takes 30 to 60 minutes, has been completed, the crucible is grasped by means of the crucible tongs (see Section **II, 37**) and gently rotated and tilted so that the molten material distributes itself around the walls of the container and solidifies there as a thin layer. This procedure greatly facilitates the subsequent detachment and solution of the fused mass. When cold, the crucible is placed in a casserole, porcelain dish, platinum basin or Pyrex beaker (according to the nature of the flux) and covered with water. Acid is added, if necessary, and the vessel is covered with a clock glass (preferably of the Fisher " speedy-vap " type), the temperature raised to 95°–100°C, and maintained until solution is achieved.

Full experimental details for effecting fusions with sodium carbonate and potassium pyrosulphate are given in Sections **IV, 70B,** and **IV, 95,** and in **IV, 94G** respectively.

II, 17. Unit of volume.—The fundamental unit employed in measuring the volume of a liquid is the litre. The **litre** *is defined as the volume occupied by one kilogram of water at the temperature of its maximum density (4°C) and subjected to normal atmospheric pressure.* It should be noted that the quantity of water which occupies one litre at 4°C has a mass of one kilogram, and *not* an apparent weight in air of one kilogram. The apparent weight in air of one litre of water at 4°C will be less than one kilogram by the buoyancy effect of the air (compare Section **II, 7**) ; if the weighing is made at the ordinary temperature, the apparent weight will be still less because of the lower density of water at temperatures above 4°C. Likewise the volume of water will depend, but to a lesser degree, upon the pressure to which it is subjected. These factors must be allowed for when determining the volume of a piece of apparatus by weighing the water that it contains or delivers.

The **millilitre** (ml.) is the thousandth part of a litre. This is the most convenient unit for expressing the capacity of volumetric glassware.

The **cubic centimetre** (c.c., c.cm., cm.^{3}) is the volume occupied by a cube each of whose edges is one centimetre in length. The most recent determinations have shown that the relationship between the millilitre and the cubic centimetre is :

$$1000 \text{ ml.} = 1000{\cdot}028 \text{ c.c.}$$

In this book the unit of volume will be taken as the millilitre in accordance with the recommendation of the National Physical Laboratory in their pamphlets of September 1924 and April 1934, and now almost universally adopted. It is true that the difference between the ml. and c.c. is only 28 parts per million and therefore well within the limits of error of most volumetric determinations ; for this reason many still use the terms c.c. and ml. synonymously. It must be remembered, however, that the ultimate unit of volume is the litre, which is based upon a determination of mass ; it is therefore more logical to adhere to the millilitre for expressing capacities.*

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* The recent discovery of deuterium oxide D_2O (" heavy water "), which has a specific gravity at 20°C of 1·1059 and a temperature of maximum

II, 18. Standard temperature.—Prior to 1934, the standard temperature in Great Britain was 15°C, but since the issue in 1934 of the " Report on Standard Temperature of Volumetric Glassware" (No. 554) by the British Standards Institution a standard temperature of 20°C has been almost universally adopted. The latter standard temperature is employed in America and on the continent of Europe. This temperature most nearly represents the average temperature of the laboratory, or at least a temperature which is readily attainable.

If we take the coefficient of cubical expansion of glass as 0·000026 ml. per ml. per degree Centigrade, the following Table gives the correction to be added when the sign is +, or subtracted when the sign is −, to or from the capacity of a 1000 ml. flask correct at 20°C in order to obtain the capacity at other temperatures.

TABLE XXVII. TEMPERATURE CORRECTION FOR 1000 ML. GLASS FLASK FOR THE EXPANSION OF GLASS (STANDARD TEMPERATURE, 20°C).

Degrees C.	5°	10°	15°	20°	25°	30°
Ml.	− 0·39	− 0·26	− 0·13	0·00	+ 0·13	+ 0·26

In the actual use of volumetric glassware for the measurements of liquids, the expansion of the liquid must also be taken into consideration if temperature corrections are to be made. Table XXVIII gives the corrections to be added or subtracted in order to obtain the volume occupied at 20°C by a volume of water which at the tabulated temperature is contained in an accurate 1000 ml. flask having a standard temperature of 20°C. It will be seen that the allowance for the expansion of water is considerably greater than that for the expansion of the glass.

II, 19. Volumetric apparatus.—The most commonly used apparatus in volumetric analysis are measuring flasks,

density of 11·6°C, introduces a complicating factor. The normal proportion of deuterium oxide in ordinary water is about 1 part in 5,000 ; this will result in a difference of about 22 parts per million in density from that of pure protium oxide H_2O. Fortunately, the proportion of deuterium oxide does not vary appreciably with all ordinary samples of water, but it is evident that a precise definition of volume must specify the proportion of this constituent.

TABLE XXVIII. TEMPERATURE CORRECTIONS FOR VOLUMES OF WATER MEASURED IN A 1000 ML. GLASS FLASK (STANDARD TEMPERATURE, 20° C).

Degrees C.	5°	10°	15°	20°	25°	30°
Correction (ml.)	+ 1·37	+ 1·24	+ 0·77	0·00	− 1·03	− 2·30

burettes, and pipettes. Graduated cylinders and weight pipettes are less widely employed. Each of these will be described in turn, together with the methods of use, calibration, and tolerances allowed by the National Physical Laboratory.

Cleaning of glass apparatus. Before describing volumetric apparatus in detail, reference must be made to the important fact that all such glassware must be perfectly clean and free from grease, otherwise the results will be unreliable. The test for cleanliness of glass apparatus is that on being filled with distilled water and the water withdrawn, only an unbroken film of water remains. If the water collects in drops, the vessel is dirty and must be cleaned. Various methods are available for cleaning. The method which is most frequently used consists in filling the apparatus with " cleaning mixture," a solution of powdered sodium or potassium dichromate in concentrated sulphuric acid, and allowing it to stand for several hours, but preferably overnight ; the acid is then poured off, the apparatus thoroughly rinsed with distilled water, and allowed to drain until dry. A more expeditious method of drying is to rinse the apparatus with pure acetone after draining off the water and then to blow or draw air through it : under no circumstances should the apparatus be heated. A more efficient cleaning liquid is a mixture of concentrated sulphuric acid and fuming nitric acid ; this may be used if the vessel is very greasy and dirty. Grease may also be removed by filling the apparatus with warm soap solution, leaving for 15 minutes, rinsing with water, followed by concentrated hydrochloric acid, and finally with distilled water.

II, 20. Measuring flasks.* A measuring flask is a flat-bottomed, pear-shaped or spherical vessel with a long narrow neck (Fig. 2–17). A thin line etched around the neck indicates the volume that it holds at a certain definite temperature, usually 20°C (both the capacity and the temperature are clearly marked on the flask) ; the flask is then said to be graduated *to contain*. Flasks with one mark are always taken *to contain* the volume specified. A flask may also be marked *to deliver* a specified volume of liquid under certain definite conditions; these are, however, not suitable for exact work. Vessels standardised at the National Physical Laboratory are marked with a letter **D** when they are meant to deliver ; if they are intended both to contain and to deliver, the letter **D** is placed above the upper mark and the letter **C** below the lower mark.

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* These are sometimes known as volumetric flasks.

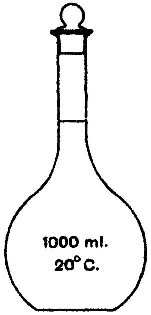

FIG. 2–17.

The mark extends completely around the neck in order to avoid errors due to parallax when making the final adjustment ; the lower edge of the meniscus should be tangential to the graduation mark, and both the front and the back of the mark should be seen as a single line. The neck is made narrow so that a small change in volume will have a large effect upon the height of the meniscus : the error in adjustment of the meniscus is accordingly small. Volumetric flasks should be fitted with ground-glass stoppers, and both the stopper and the flask should be numbered.

Measuring flasks are ordinarily made of 50, 100, 250, 500, 1000, and 2000 ml. capacity. They are employed in making up standard solutions to a given volume ; they can also be used for obtaining, with the aid of pipettes, aliquot portions of the substance to be analysed.

Calibration. A large balance, which will carry about a kilogram in each pan and which has a sensitivity when fully loaded of about 5 mg., is required. The flask is first thoroughly cleaned and dried ; it is then weighed on the large balance. The flask is then filled with distilled water, which has been standing in the balance room for at least an hour before use, to a few millimetres above the mark : care is taken to avoid wetting the neck above the water surface. The lowest point of the water meniscus is then adjusted to the graduation mark by withdrawing small quantities of water with a capillary tube or with a narrow tube drawn out to a jet at the lower end. The flask is then weighed,* and the temperature of the water noted. The true volume of the water filling the flask to the graduation mark can be calculated with the aid of the following Table. The values in the Table have been obtained by making allowance for (*a*) the difference in volume of the glass vessel at the calibration temperature and at 20°C, (*b*) the density of water at the temperature of the calibration, and (*c*) the effect of buoyancy of the air upon the water and the brass weights. The figures apply to an atmospheric pressure of 760 mm. of mercury and a relative humidity of the air of 50 per cent ; the usual deviation from these figures will affect the buoyancy correction (compare Section **II, 7**) only slightly and can be neglected for most purposes.

TABLE XXIX. WEIGHT OF WATER (BRASS WEIGHTS IN AIR) TO GIVE ONE LITRE AT 20°C.

Temp. (°C)	*Weight* (*g.*)	*Volume of 1 g. of water* (*ml.*)	*Temp.* (°C)	*Weight* (*g.*)	*Volume of 1 g. of water* (*ml.*)
10°	998·39	1·0016	23°	996·60	1·0034
11°	998·32	1·0017	24°	996·38	1·0036
12°	998·23	1·0018	25°	996·17	1·0038$_5$
13°	998·14	1·0018$_5$	26°	995·93	1·0041
14°	998·04	1·0019	27°	995·69	1·0043
15°	997·93	1·0021	28°	995·44	1·0046
16°	997·80	1·0022	29°	995·18	1·0048
17°	997·66	1·0023	30°	994·91	1·0051
18°	997·51	1·0025	31°	994·64	1·0054
19°	997·35	1·0026	32°	994·35	1·0057
20°	997·18	1·0028	33°	994·06	1·0060
21°	997·00	1·0030	34°	993·75	1·0063
22°	996·80	1·0032	35°	993·45	1·0066

Note. For the calibration of flasks of capacity other than 1 litre, the corresponding multiple or sub-multiple of the above values is taken.

If the error, calculated with the aid of Table XXIX, falls within the limits of tolerance of " Class A " apparatus (see following paragraph), the flask may be taken as accurate for all ordinary quantitative work. If, however, the error is large, the simplest procedure is either to affix a small paraffined label to the flask bearing the true capacity and the date of calibration, or to calibrate another flask. The process of re-graduating the flask is best left to the manufacturers.

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* If a precision type of balance is not available, or the equality of the length of the balance arms is suspect, it is best to weigh by the method of substitution (Section **II, 6C**). Counterpoise the empty flask either by adding lead shot into a beaker placed on the right-hand pan and/or another set of weights : observe the rest point. Remove the flask and replace it by weights sufficient to bring the balance to the same rest point. Record the weight, and remove both weights and tare. Weigh the flask filled with distilled water to the mark by the method of substitution as before. The difference in weights on the left-hand pan will give the weight of the water.

Standardised flasks. Measuring flasks which have been verified at the National Physical Laboratory can be purchased. The N.P.L. recognise two types of volumetric glassware: those which have passed " Class A " tests (marked **NB.A.**) and those which have passed " Class B " tests (marked **NB.B.**). The former are designed for vessels intended to possess the high accuracy normally required for scientific use; the latter are intended for ordinary routine or commercial analysis. Apparatus which has passed the " Class A " tests can also be supplied with a certificate giving the exact volume; these may be employed in work demanding the highest accuracy. Full details concerning the construction and design of volumetric glassware are given in the pamphlet issued by the N.P.L. in April 1934.* Only the tolerances or permissible errors for flasks " to contain " will be given here.

Capacity, ml.		25	50	100	250	500	1000	2000
Tolerance, ± ml.	*"Class A"*	0·03	0·04	0·06	0·1	0·15	0·2	0·4
	"Class B"	0·04	0·06	0·1	0·2	0·3	0·4	0·6

II, 21. Pipettes.—Pipettes are of two kinds: (i) those which have one mark and *deliver* a small, constant volume of liquid under certain specified conditions (**transfer pipettes**); (ii) those in which the stems are graduated and are employed to deliver various small volumes at discretion (**graduated** *or* **measuring pipettes**). They are shown in Fig 2–18 as *A* and *C*; type *B* is a useful form which is employed for measuring out corrosive liquids, the bulb preventing the entrance of liquid into the mouth. Graduated pipettes are useful for measuring out volumes of liquids approximately; they are not employed in exact work.

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* The U.S. Bureau of Standards issue a similar pamphlet (Circular No. 9 for 1916). Only one type of apparatus, corresponding roughly to the N.P.L. " Class A " is, however, allowed.

Transfer pipettes are constructed with capacities of 1, 2, 5, 10, 20, 25, and 50 ml.; those of 10, 25, and 50 ml. capacity are most frequently employed. In using such pipettes, they are first rinsed with the liquid, then filled by suction to about 1–2 cm. above the mark, and the upper end of the pipette is closed with the tip of the dry index finger; any adhering liquid is wiped from the outside of the lower stem. The liquid is allowed to run out slowly by slightly relaxing the pressure of the finger and by carefully rotating the pipette until the bottom of the meniscus just reaches the graduation mark; the pipette must be held vertically so that the mark is at the same level as the eye. Any drops adhering to the tip are removed by stroking against a glass surface. The liquid is then allowed to run into the receiving vessel, the tip of the pipette touching the wall of the vessel. When the continuous discharge has ceased, the jet is held in contact with the side of the vessel for 15 seconds (**draining time**). At the end of the draining time, the receiving vessel is removed from contact with the jet of the pipette, thus removing any drop adhering to the outside of the pipette. The liquid remaining in the jet of the pipette must not be removed either by blowing or by other means; blowing may introduce grease from the mouth. The above standard procedure for filling and emptying a pipette is that recommended by the National Physical Laboratory, and will be employed in its calibration.

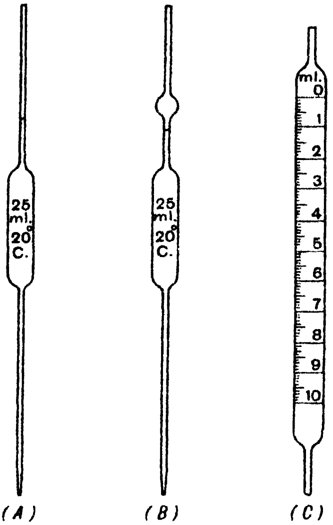

FIG. 2-18.

A pipette will not deliver constant volumes of liquid if discharged too rapidly. The orifice must be of such size that the time of outflow is about 20 seconds for a 10 ml. pipette, 30 seconds for a 25 ml. pipette, and 35 seconds for a 50 ml. pipette.

Calibration. The pipette is cleaned by filling it with dichromate-sulphuric acid cleaning mixture and allowing it to stand, preferably overnight. Filling is effected by attaching

C (Fig. 2–20) burettes are generally employed for titrating hot solutions; the heat will not reach the bulk of the solution in the burette and thus will not affect its volume. Burettes are usually of 50 ml. capacity graduated to tenths of a ml.: capacities of 10 ml. and 25 ml. are also available. *Burettes are employed to deliver variable volumes of liquid.*

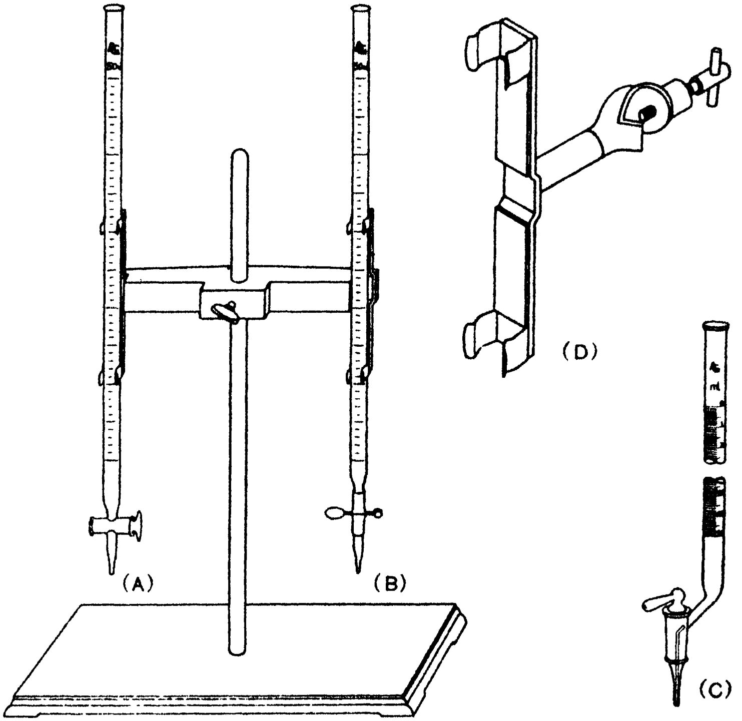

Fig. 2–20.

The mode of use is as follows. The clean, empty burette is fixed into a suitable stand and clamped vertically.* About 10 ml. of the solution to be employed is poured into it so as to wet the whole internal surface, and is then run completely out ; this rinsing is repeated. The burette is then filled to a little above the highest graduation ; if a short funnel is used, it must be removed *immediately* after the filling. The liquid is then allowed to flow out until the lowest point of the meniscus just touches this graduation ; the jet must of course be completely full of liquid. To read the position of the meniscus, the eye must be at the same level as the meniscus in order to avoid errors due to parallax. In the best type of burette, the graduations are carried completely round the tube for each ml. and half-way round for the other graduation marks : parallax is thus easily avoided. To aid the eye in reading the position of the meniscus a piece of white paper or cardboard, the lower half of which is blackened either by painting with dull black paint or by pasting a piece of dull black paper upon it, is employed. When this is placed so that the sharp dividing line is 1 to 2 mm. below the meniscus, the bottom of the meniscus appears to be darkened and is sharply outlined against the white background (Fig. 2–21)* ; the level of the liquid can then be accurately read. For all ordinary purposes readings are made to 0·05 ml. ; for precision work readings to 0·01–0·2 ml. (by estimation with the aid of a lens) should be made.

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* Of the many stands on the market the "Technico" burette holder (Registered Design, No. 830030), illustrated in Fig. 2-20 (burettes *A* and *B* are held in position by this double clamp), is very convenient and also inexpensive. No parts of the holder obscure graduation lines or numbers on the burette, and the burette is held firmly in a truly vertical position. The movement of the burette in order to bring the meniscus to eye level is but the work of a moment. A single burette holder, which can be fixed on a retort stand (Fig. 2-20, *D*), is also marketed. These burette holders may be purchased from the sole manufacturers, Messrs. A. Gallenkamp and Co., Ltd., 17–29 Sun Street, Finsbury Square, London, E.C.2, England.

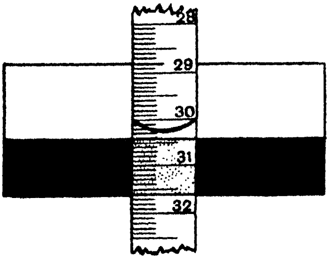

Fig. 2–21.

The so-called Schellbach burette, which contains a white enamelled band, with central blue ribbon, fused vertically at the back of the burette tube, was originally intended to improve the ease of reading the level of the liquid and also to eliminate parallax. Its use in practice is not, however, very satisfactory (such burettes are admitted to only class " B " tests at the N.P.L.), and hence cannot be recommended.

As a general rule, it is advisable to use the zero mark each time. It has been established that practically no after-drainage takes place in a burette if the rate of outflow does not exceed a certain speed. If the speed is exceeded, owing to the jet being too large, then drainage takes place for several minutes. The limits for the time of outflow with the tap fully open and the jet not in contact with the receiving vessel are given in connexion with the N.P.L. "Class A" tests in a subsequent paragraph. A burette should be selected which conforms to these limits. The drop adhering to the jet after the liquid has been discharged is removed by bringing the side of the receiving vessel into contact with the jet. When not in use, burettes should be well rinsed with distilled water and covered with a short inverted test-tube to keep out dust, or they may be inverted in the burette stand, jet uppermost.

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* A celluloid black and white disc, which can be slipped over the burette is available commercially (*e.g.* " Fisher " burette meniscus holder, " Baird and Tatlock " burette reader, etc.).

Burettes fitted with rubber and a pinch cock are used for alkaline solutions and as cheap substitutes for glass stop-cock burettes; they cannot be employed for such solutions as potassium permanganate and iodine, which attack rubber. The use of any form of burette other than that fitted with a glass stop-cock is not recommended for the following reasons: (i) some of the liquid may attack the rubber, and (ii) it is impossible to see whether the air has been completely displaced in the rubber tube. Alkaline solutions, including those of caustic alkalis, may be used with glass taps, but the burettes must be emptied and washed immediately after use, otherwise the taps are liable to stick. Where the use of alkaline solutions in a burette is a routine process, it is best to utilise a nickel or silver stop-cock.

Lubricants (or greases) for glass stop-cocks. The simplest lubricant is either pure vaseline or a mixture of pure vaseline and resin cerate.

A "soft" grease may be prepared by thoroughly mixing, by melting and stirring, 1 part of beeswax and 3 parts of pure vaseline. A "hard" grease is obtained by adding 1 part of soft black rubber in small pieces to the latter mixture, heating to 140° to 150°C, and stirring continuously until thoroughly incorporated.

An excellent lubricant (Shepherd, 1931), which is particularly suitable for gas analysis apparatus, is obtained from 6 parts of rubber (pale crêpe, freshly milled, and free from dirt and lint), 7 parts of white vaseline and 1 part of paraffin wax, m.p. 40° to 45°C. The vaseline and paraffin wax are melted in a large porcelain casserole and the rubber is added in several portions. The mixture is placed in a thermostated oven or in an air bath (Section **II, 12F**; first paragraph) and stirred continuously for 190 hours at 155° to 165°C. It is then transferred to 2 oz. ointment jars and chilled in ice immediately, care being taken to prevent condensation of water on the grease.

Excellent lubricants may be purchased.*

Calibration of a glass-stoppered burette. The burette is filled with dichromate-sulphuric acid cleaning mixture and a beaker placed beneath the burette. The burette is allowed to stand for one hour, but preferably overnight. The solution is run out and the burette rinsed five or six times with distilled water. The stop-cock and the inside of the ground joint are then wiped dry ; the stop-cock is then smeared lightly with a suitable lubricant, replaced into position, and turned several times in order to spread the lubricant evenly in the ground joint. The burette is then clamped vertically and filled with distilled water ; the latter should have been standing for at least an hour prior to use so as to be certain that it has acquired the room temperature. The temperature of the water is noted. The air in the jet is expelled by running out water from the burette. Two methods are available for the actual calibration. The first is based upon that employed at the National Physical Laboratory. The second is due to Ostwald ; it is very convenient to use, but is not accepted by the N.P.L.

Method 1. The burette is filled with water to a short distance above the zero mark and water is slowly run out until the meniscus is exactly on the zero mark. The drop of water adhering to the jet is removed by bringing the jet into contact with the side of the beaker. For reading the position of the meniscus to 0·01 ml., the device shown in Fig. 2–21 coupled, preferably, with a lens, may be employed. In the better quality burette in which the calibrations are carried completely round for the 1 ml. divisions and half round for fractions of a ml., errors due to parallax may be avoided by placing the eye so that the front and back of the graduation at the meniscus appear to coincide. The burette is allowed to deliver freely, *i.e.*, with the stop-cock fully open, into a clean, weighed Erlenmeyer (conical) flask of 100–150 ml. capacity. When the meniscus of the water is approximately 1 cm. from the line to be tested, the rate of outflow is reduced so that the motion of the water surface is brought under complete control ; the meniscus is adjusted exactly on the mark.* No period of waiting for drainage should be allowed. The drop adhering to the jet after the setting has been made is removed by bringing the side of the flask into contact with the jet. The flask is then stoppered and weighed to the nearest 0·01 g. This procedure is followed for each of the graduations to be tested, *e.g.*, at 5 ml. intervals, 5, 10, 15, 20, etc., or at 10 ml. intervals. The zero mark is always taken as the starting point, since a very small drainage error might take place between the readings and effect the accuracy of the intermediate determinations. The whole process should be repeated ; the duplicate determinations should agree within 2 centigrams. The volume actually delivered is calculated from the weight of the water and the volume of 1 g. of water at the temperature of the calibration given in Table XXIX. The results should be tabulated as follows.

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* A variety of lubricants is supplied by W. Edwards and Company, Vaughan Road, London, S.E.5, England.

CALIBRATION OF A BURETTE. (TEMPERATURE = —°C).

Burette readings (ml.)	*Weight of Water delivered (mean)*	*True volume at 20°C*	*Correction (ml.)*
0·00– 5·00	– g.	– ml.	– ml.
0·00–10·00	– g.	– ml.	– ml.
0·00–15·00	– g.	– ml.	– ml.
0·00–20·00, etc.	– g.	– ml.	– ml.

The results may also be plotted graphically with burette readings (1 ml. = 2 mm.) as abscissae and corrections (0·01 ml. = 2 mm.) as ordinates.

Method 2. The so-called **burette-calibrator** is employed. This consists of a small pipette (usually of 2 ml. capacity) with a mark on the upper and lower limbs, and a tap and side tube fused to the lower end. It is first thoroughly cleaned and then attached by means of a short piece of stout rubber tubing ("pressure tubing") to the jet of the burette (Fig. 2-22); both burette and pipette are clamped vertically. The tap of the pipette is closed and distilled

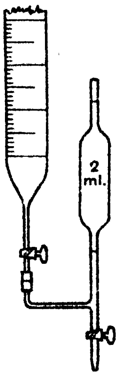

FIG. 2–22.

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* If this has been missed by a small amount, the volume is read to the nearest 0·01 ml.

water is run in from the burette until its level is about 2 cm. above the upper mark. If all air bubbles have not thus been removed from the pipette and its jet, more water is run in and the adjustment repeated. The drop of water adhering to the jet is removed by bringing it into contact with the inside wall of a beaker. The jet is then placed against the side of a tared weighing bottle or a small stoppered flask, and water is allowed to flow slowly from the burette-calibrator until the meniscus reaches the lower mark ; the bottle or flask is stoppered and reweighed. This process is repeated at least six times, and the mean weight of the water delivered is obtained. The exact volume of the pipette can then be calculated from the known temperature of the water and Table XXIX.

The burette is now filled, adjusted exactly to the zero mark by connexion with the pipette, and the latter, in turn, adjusted to its lower mark. The pipette is then filled to the upper mark from the burette, and the reading of the latter taken. The pipette is emptied to the lower mark, and the process repeated so that successive readings are taken at *ca.* 2, 4, 6, 8, ... 50 ml. marks on the burette. From the known volume of the burette-calibrator (say, 1·9962 ml.), the correct volumes at the successive readings of the burette can be computed and the corrections thus evaluated. The final values may be collected in the form of a table or plotted graphically as described under *Method 1.*

Standardised burettes. The National Physical Laboratory recognises two types of tests for burettes, *viz.*, " Class A " and " Class B." For the former, only burettes with glass taps are admitted : if a filling tube is sealed in between the lowest graduation mark and the tap, a stop-cock must be present in the filling tube. Various details as to the construction of burettes are to be found in the pamphlet " Tests on Volumetric Glassware " (N.P.L., April 1934), but the tolerances and times of outflow (the latter are important in connexion with the drainage error) are tabulated below.

Total capacity, ml.	2	10	30	50	100	200
Maximum error, ± ml., " Class A "	0·01	0·02	0·03	0·06	0·1	0·2
Maximum error, ± ml., " Class B "	0·02	0·04	0·06	0·1	0·2	0·4

The tolerances apply to the whole of the graduated portion and to any portion of it; the differences in errors between any two points must not exceed these values.

Length graduated, cm.	20	30	40	50	60	70
Time of outflow limits, seconds, "Class A"	40-75	60-105	80-135	100-165	120-195	140-225
Time of outflow limits, seconds, "Class B"	30-75	40-105	55-135	70-165	80-195	95-225

Only burettes which conform to "Class A" tests are suitable for use in work of the highest accuracy and as standards. The N.P.L. will, on payment of a certain fee, give a certificate showing the exact volume delivered at various graduations on "Class A" burettes.

II, 23. Weight burettes.—For work demanding the highest possible accuracy in transferring various quantities of liquids, weight burettes are employed. As their name implies, they are weighed before and after a transfer of liquid. A very useful form is shown diagrammatically in Fig. 2–23, *a*. There are two ground-glass caps, the lower one is closed, whilst the upper one is provided with a capillary opening; the loss by evaporation is accordingly negligible. For hygroscopic liquids, a small ground-glass cap is fitted to the top of the capillary tube. The burette is roughly graduated in 5 ml. intervals.

The Lung-Rey pipette is shown in Fig. 2–23, *b*. There is a small central bulb (5 to 10 ml. capacity) closed by two stop-cocks **1** and **2**; the pipette **3** below the stop-cock has a capacity of about 2 ml., and is fitted with a ground-on test tube **4**. This pipette is of particular value for the weighing

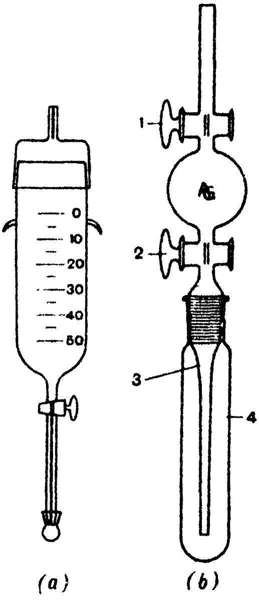

FIG. 2–23.

out of corrosive and fuming liquids (see Section **III, 12**).

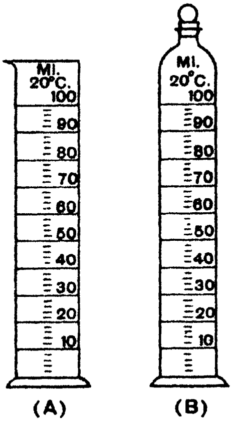

FIG. 2-24.

II, 24. Graduated cylinders.*—These are graduated vessels of thick glass (Fig. 2-24), and are available in capacities from 2 ml. to 2000 ml. Since the area of the upper surface of the liquid is much greater than in a measuring flask, the accuracy is not very high. Graduated cylinders cannot therefore be employed for work demanding even a moderate degree of accuracy. They are, however, useful where only rough measurements are required. Two kinds are generally employed: the wide-mouthed, open type with spout (Fig. 2-24, *A*) and the stoppered type (Fig. 2-24, *B*). They may be calibrated, if desired, by measuring into them definite volumes of water from calibrated burettes or pipettes.

II, 25. Storage and preservation of solutions in volumetric analysis.—Solutions, which are comparatively stable and unaffected by exposure to air, may be stored in whole or half winchester quart bottles; for work requiring the highest accuracy Pyrex, or other resistance glass, bottles fitted with ground-glass stoppers should be employed, the solvent action of the solution being thus considerably reduced. The bottle should be clean and dry: a little of the stock solution is introduced, the bottle well rinsed with this solution, drained, and the remainder of the solution poured in and the bottle immediately stoppered. If the bottle is not dry, but has recently been thoroughly rinsed with distilled water, it may be rinsed successively with three small portions of the solution and drained well after each rinsing; this procedure is, however, less satisfactory than that employing the clean and dry vessel. Immediately after the solution has been transferred to the stock bottle, it should be labelled with (1) the name of the solution, (2) its concentration, (3) the date of preparation, and (4) the initials of the person who prepared the solution, together with any other relevant data. Unless the bottle is completely filled, internal evaporation and condensation will cause drops of water to form on the upper part of the inside of the vessel. For this reason, the bottle must be thoroughly shaken before removing the stopper.

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* Also known as measuring cylinders.

Solutions which are liable to alter their strength by access of air (*e.g.*, alkali hydroxides, ferrous ammonium sulphate, titanous chloride or sulphate) may be kept in the apparatus shown diagrammatically in Fig. 2-25, *a*. The burette has a three-way tap which enables it either to be filled from the stock bottle or to be emptied. If such a burette is not available, one with a side-tube and stop-cock (Fig. 2–25, *b*) will serve equally well. The tube **T** is permanently connected with a source of hydrogen (*e.g.*, from a Kipp's apparatus) if the solution is oxidised upon exposure to air (*e.g.*, ferrous sulphate, ferrous ammonium sulphate, titanous chloride or sulphate), or to a soda-lime guard tube, if it contains caustic alkali. In the latter case, particularly if ordinary glass vessels are used, the solution may become contaminated with silicates owing to the attack of the alkali on the glass ; it is better to employ a Jena glass storage vessel, or the inside of the vessel may be coated with a thin layer of paraffin wax or with " thermoprene."*

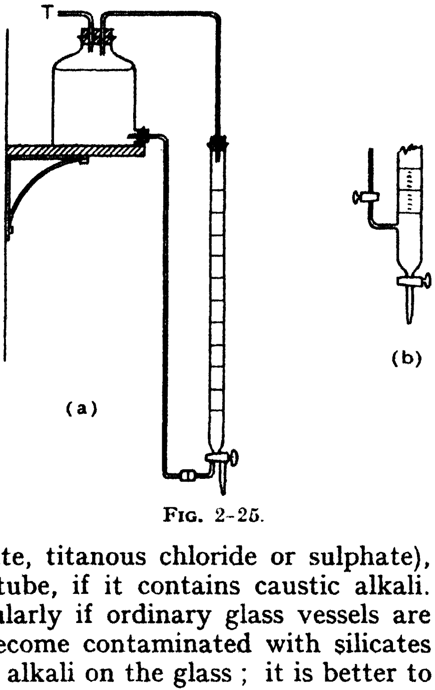

Fig. 2-25.

An apparatus for the storage of large volumes of solutions which alter their strength upon exposure to air, *e.g.*, ferrous sulphate solution, and which permits of the automatic filling of the burette has been designed by Zintl and Reinäcker (1926). A modification, due to G. F. Smith (1935), is shown in Fig. 2-26. **A** is a large storage bottle of 10 to 15 litres capacity. **B** is a 50 ml. burette provided with an automatic filling device at **C** (the point of the drawn-out tube is adjusted to be exactly at the zero mark of the burette), **D** is the burette-bottle clamp, **E** is a two-holed rubber stopper, **F** is a ground glass tension joint, **G** is a rubber tube connected to a source of hydrogen (for example, a Kipp's apparatus), **H** is a Bunsen valve, and **J** is hydrogen. The burette is filled by closing tap **K** and passing hydrogen through **G** ; tap **L** is then closed, tap **K** opened, and the excess of liquid allowed to siphon back.

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* This is a rubber paint made by the B. F. Goodrich Company, Akron, Ohio, U.S.A.

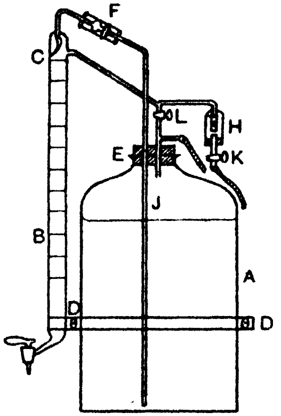

FIG. 2-26.

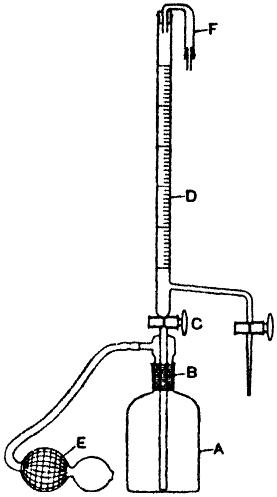

FIG. 2-27.

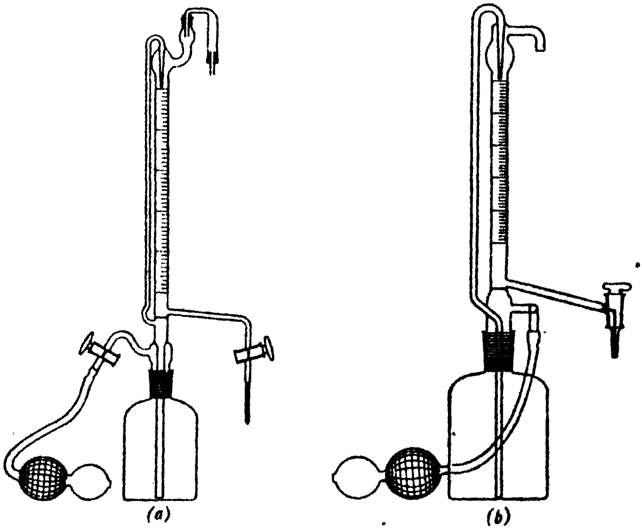
(a)
(b)

FIG. 2-28.

Two other apparatus* for the storage of standard solutions are shown in Figs. 2-27 and 2-28. These are adaptations of micro-apparatus to the macro scale. Fig. 2-27 is self-explanatory. The solution is contained in the storage bottle **A** and the 50 ml. burette is fitted into this by means of a ground-glass joint **B.** To fill the burette, tap **C** is opened and the liquid pumped into the burette by means of the small bellows **E.** **F** is a small guard tube ; this is filled with soda-lime or " sofnolite " when caustic alkali is contained in the storage bottle. Bottles with a capacity up to 2 litres are provided with standard ground-glass joints ; large bottles, up to 15 litres capacity, can also be obtained. Fig. 2-28, *a* and *b* portrays similar apparatus, but with an automatic filling device. The solution is pumped into the burette and enters it through a glass tube which terminates in a capillary exactly at the zero mark ; immediately the pressure is released, the solution above the zero mark is automatically siphoned back into the storage bottle.

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* Obtainable from A. Gallenkamp and Co. Ltd., 17–29 Sun Street, Finsbury Square, London, E.C.2, England.

TECHNIQUE OF GRAVIMETRIC ANALYSIS

The apparatus and operations common to both volumetric and gravimetric analysis have been discussed in the preceding Sections, as has also the general theory underlying gravimetric analysis. The experimental technique peculiar to analysis by weight will be considered in the following pages.

The operations of gravimetric analysis may be summarised under the headings: (*a*) precipitation, (*b*) filtration, (*c*) the washing of the precipitate, and (*d*) the drying, ignition and weighing of the precipitate.

II, 26. Precipitation.—The conditions for precipitation are given in Section **I, 59.** Precipitations are usually carried out in resistance glass beakers and the solution of the precipitant is added slowly (for example, by means of a pipette, burette or tap funnel) and with efficient stirring of the suitably diluted solution. The addition must always be made without splashing; this is best achieved by allowing the solution of the reagent to flow down the side of the beaker or precipitating vessel. Only a moderate excess of the reagent is generally required; a very large excess may lead to increasing solubility (compare Section **I, 10**) or contamination of the precipitate. After the precipitate has settled, a few drops of the precipitant should always be added to determine whether further precipitation occurs. As a general rule, precipitates are not filtered off immediately after they have been formed; most precipitates, with the exception of those which are definitely colloidal, such as ferric hydroxide, require more or less digestion (Section **I, 58**) to complete the precipitation and make all particles of filterable size. In some cases digestion is carried out by setting the beaker aside and leaving the precipitate in contact with the mother liquor at room temperature for 12 to 24 hours; in others, where a higher temperature is permissible, digestion is usually effected near the boiling point of the solution. Hot plates, water baths, or even a low flame if no bumping occurs, are employed for the latter purpose; in all cases the beaker should be covered with a clock glass with the convex side turned down or, if available, with a Fisher " speedy-vap " beaker cover. If the solubility of the precipitate is appreciable, it may be necessary to allow the solution to attain room temperature before filtration.

II, 27. Filtration.—This operation is the separation of the precipitate from the mother liquor, the object being to get the precipitate and the filtering medium quantitatively free from the solution. The media employed for filtration are: (1) filter paper; (2) filter mats of purified asbestos (Gooch crucibles) or of platinum (Munroe crucibles); (3) porous plates of glass (Jena sintered glass filtering crucibles), of quartz (Jena sintered quartz filtering crucibles) or of porcelain (porous porcelain filtering crucibles). The choice of the filtering medium will be controlled by the nature of the precipitate (filter paper is especially suitable for gelatinous precipitates and for those which must be heated to a very high temperature before weighing) and also by the question of cost. The latter is of great importance in laboratories where the number of students is large and departmental grants small. The limitations of the various filtering media are given in the account which follows.

II, 28. Filter papers.—Quantitative filter papers must have a very small ash content; this is achieved during manufacture by washing with hydrochloric and hydrofluoric acids. The sizes generally used are circles of 7·0, 9·0, 11·0, and 12·5 cm. diameter, those of 9·0 and 11·0 cm. being most widely employed. The ash of a 11 cm. circle should not exceed 0·0001 gram; if the ash exceeds this value, it should be deducted from the weight of the ignited residue. Manufacturers give values for the average ash per paper: the value may also be determined, if desired, by igniting several filter papers in a crucible. Quantitative filter paper is made of various degrees of porosity. The filter paper used must be of such texture as to retain the smallest particles of precipitate and yet permit of rapid filtration. Three textures are generally made, one for very fine precipitates, a second for the average precipitate which contains medium sized particles, and a third for gelatinous precipitates and coarse particles. The speed of filtration is slow for the first, fast for the third, and medium for the second. Hardened filter papers are made by treating quantitative filter papers with nitric acid; these have an extremely small ash, a much greater mechanical strength when wet, and are more resistant to acids and alkalis. They are strongly recommended for use in all quantitative work.

The author has found "Whatman" filter papers very satisfactory in practice; the characteristics of the chief varieties suitable for quantitative work are collected in the following Table* ; the ashes for the two most frequently used sizes, 9 cm. and 11 cm., are included.

TABLE XXX. "WHATMAN" QUANTITATIVE FILTER PAPERS.

Filter Paper.	*Fast speed. Retain coarse particles.*	*Medium speed. Retain medium-sized particles.*	*Slow speed. Retain fine particles.*
Single acid (HCl) washed	No. 31	No. 30	No. 32
Ash (mean) 9 cm.	0·00022 g.	0·00021 g.	0·00021 g.
11 cm.	0·00033 g.	0·00031 g.	0·00031 g.
Hardened single acid washed	No. 531	No. 530	—
Ash (mean) 9 cm.	0·00013 g.	0·00014 g.	—
11 c.m	0·00019 g.	0·00021 g.	—
Double acid (HCl, HF) washed	No. 41	No. 40	No. 42
Ash (mean) 9 cm.	0·000102 g.	0·000090 g.	0·000060 g.
11 cm.	0·000152 g.	0·000134 g.	0·000089 g.
Hardened double acid washed	No. 541	No. 540	No. 542
9 cm.	0·000042 g.	0·000045 g.	0·000051 g.
11 cm.	0·000062 g.	0·000067 g.	0·000076 g.

The filter papers Nos. 30–32 and 530–531 are comparatively cheap and may be used for elementary students. For precise quantitative work, Nos. 40–42 or, preferably, the hardened variety Nos. 540–542, which have a greater mechanical strength and a greater resistance to acids and alkalis, should be employed. Nos. 41 and 541 are used for gelatinous and flocculent precipitates, and Nos. 40 and 540 for most other precipitates encountered in quantitative analysis.

The size of the filter paper selected for a particular operation is determined by the bulk of the precipitate and not by the volume of the liquid to be filtered. The entire precipitate should occupy about a third of the capacity of the filter at the end of the filtration. As already pointed out, filter papers of 9 cm. and 11 cm. diameter find the most frequent use.

A funnel with an angle as nearly 60° as possible should be employed ; the stem should have a length of about 15 cm. in order to promote rapid filtration. The filter paper must be carefully fitted into the funnel so that the upper portion beds tightly against the glass. Some analysts recommend that the filter paper should rest completely against the wall of the funnel ; this is really unnecessary since a filter paper which adheres snugly to the funnel over the upper half will permit of more rapid filtration. To prepare the filter paper for use, the dry paper is usually folded exactly in half and exactly again in quarters. The folded paper is then opened so that a 60° angle cone is formed with three thicknesses of paper on the one side and a single thickness on the other ; the paper is then adjusted to fit the funnel. The paper is placed in the funnel, moistened thoroughly with water, pressed down tightly to the sides of the funnel either with the clean forefinger or with a flattened glass rod, and then filled with water. If the paper fits properly, the stem of the funnel will remain filled with liquid during the filtration. Another method of folding the filter which is preferable to that just described consists in folding the paper across a diameter and then once again so that the two halves of the first crease do not quite coincide (the two extreme edges should enclose an angle of 3° to 4° for a 60° funnel) ; the corner of the fold should be torn off to a depth of about one-third of the radius of the paper (Fig. 2-29). When this filter is opened and placed in the funnel, it should fit the walls tightly at the upper half : if it does not fit properly, the angle of the second fold must be adjusted until it does. Here also, the ultimate test of a proper fit, is that the stem of the funnel remains filled with liquid throughout the filtration. It must be emphasised that a funnel of proper size must be used : the top of the filter paper when set in the funnel should be about 1 cm. below the rim of the latter.

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* Compiled from the pamphlet issued by the manufacturers, W. and R. Balston Ltd., Maidstone, England.

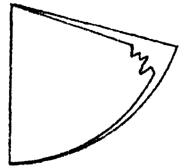

Fig. 2-29.

To carry out a filtration, the funnel containing the properly fitted paper is placed in a funnel stand (or is supported vertically in some other way) and a clean beaker placed so that the stem of the funnel just touches the side; this will prevent splashing. The liquid to be filtered is then poured down a glass rod into the filter, directing the liquid against the side of the filter and not in the apex (Fig. 2-30): the lower end of the stirring rod should be very close to, but should not quite touch,

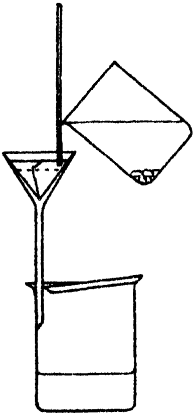

Fig. 2-30.

the filter paper on the side having three thicknesses of paper. The paper is never filled completely with the solution ; the level of the liquid should not rise closer than to within 5 to 10 mm. from the top of the paper. Any precipitate which adheres firmly to the side of the beaker or to the stirring rod may be removed with a rubber-tipped rod or " policeman " (Section **II, 10L**).

Filtration may be appreciably accelerated by the use of the Jena " analytical funnels " or the similar Pyrex 60° funnels. These funnels have an exact angle of 60°, possess a stem 100 to 150 mm. long with an internal diameter of 3 mm., and are specially grooved to permit of rapid filtration. Filtration by suction with a filter paper (for apparatus, see Section **II, 31**) is rarely necessary : with gelatinous and some finely-divided precipitates, the suction will draw the particles into the pores of the paper and the speed of filtration will actually be reduced rather than increased. If suction is used with filter paper, it is necessary to support the paper in a perforated cone made of platinum (" filter cone ") or in a " Whatman " filter cone (hardened, No. 51).

II, 29. Macerated filter paper.—Dittrich (1904) first recommended the use of the filter paper pulp as an aid in the filtration and washing of gelatinous or slimy precipitates, which tend to clog the pores of ordinary filter paper. The macerated paper may be prepared by vigorously shaking an ordinary quantitative filter paper, torn into small pieces, with hot distilled water in a stoppered conical flask until it is disintegrated to a pulp. This is unnecessary as macerated filter paper tablets may be purchased ready for use. Two types are available : the first, known as Whatman " accelerators," is in the form of oblong pieces ($1'' \times \frac{3}{4}'' \times \frac{1}{16}''$), each weighing about 0·33 g. and giving an ash of about 0·000036 g. ; the second, known as Whatman " ashless tablets," is in the form of discs (4·25 cm. diameter and about 4 mm. thickness), each weighing about 2·28 g. and giving an ash of about 0·00025 g. Either one or two accelerators or a quarter of a tablet is used in the average precipitation ; these disintegrate readily when placed in water. The bulk of the macerated filter paper should be approximately equal to that of the gelatinous precipitate. The macerated filter paper is added *after* the precipitate has formed and *immediately before* filtration. When the bulk of the precipitate and paper is large, it is usually advisable to support the filter paper on a Whatman filter cone (hardened, No. 51), and drain well on the pump upon completion of the washing. It is best not to dry the filter and precipitate completely as a hard mass may be formed, which is difficult to insert in the crucible in the subsequent ignition. It should be transferred while still slightly moist to the crucible, and the drying completed in the crucible by heating over a very small luminous flame. Alternatively, the wet mass may be ignited in a silica crucible, preferably of the Main Smith form (see Section **II, 35B**).

Macerated filter paper is also useful when it is desired to clarify a solution containing a finely divided precipitate that is difficult to coagulate.

II, 30. Filter mats. Gooch crucibles.—F. A. Gooch (1878) first employed a filter mat of purified asbestos ; this was supported inside a tall-form platinum crucible, the bottom of which was perforated with numerous small holes. Subsequently the idea was extended to porcelain crucibles, and in recent years to silica crucibles. All crucibles of this type are now termed Gooch crucibles. The porcelain type is the most widely used for student and routine work. When the term Gooch crucible is employed in this book, the porcelain variety must be understood ; crucibles of platinum and of silica will be called platinum Gooch crucibles and silica Gooch crucibles respectively. The asbestos must be carefully selected and prepared : the long fibred, amphibole asbestos is the most suitable. Gooch specified " white, silky, anhydrous asbestos." The tedious process of preparing the asbestos by boiling with hydrochloric acid, etc., is now usually carried out by chemical manufacturers. " Asbestos for Gooch crucibles " may be purchased at a reasonable price from any firm of repute, and used with confidence. When such asbestos is shaken with water, it should separate into very small fibres ; no undisintegrated asbestos should be present. All Gooch crucibles are used under suction, and require holders and receivers that are strong enough to withstand a partial vacuum. These are described in the following paragraph.

II, 31. Preparation of a Gooch crucible.—The Gooch crucible (Fig. 2-31, *A*) is usually supported in a special holder, known as a Gooch funnel, by means of a wide rubber tube (Fig. 2-31, *B*) ; the bottom of the crucible should be quite free from the side of the funnel and from the rubber gasket, the latter in order to be quite sure that the filtrate does not come into contact with the rubber. The Gooch funnel passes through a one-holed rubber bung into a large filter flask of about 750 ml. capacity. The tip of the funnel must project below the side arm of the filter flask so that any risk that the liquid may be sucked out of the filter flask may be avoided. The filter flask should be coupled with another flask of similar capacity, and the latter connected with a water filter pump ; if the water in the pump should " suck back," it will first enter the empty flask and the filtrate will not be contaminated. It is advisable also to have some sort of pressure regulator to limit the maximum pressure under which filtration is conducted. A simple method is to insert a glass tap in the second filter flask, as in Fig. 2-31, *B* ; alternatively, a glass T piece may be introduced between the receiver and the pump, and one arm closed either by a glass tap or by a piece of heavy rubber tubing (" pressure " tubing) carrying a screw clip. For some work it is convenient to collect the filtrate directly in a beaker : this may be done by means of the apparatus shown in Fig. 2-32. It consists of a bell jar resting upon a ground-glass plate and provided with tubulures at the top and side, a three-way tap is attached to the side tubulure so that suction is easily applied or stopped. Here also it is advisable to provide a trap to protect the filtrate from the back flow from the pump.

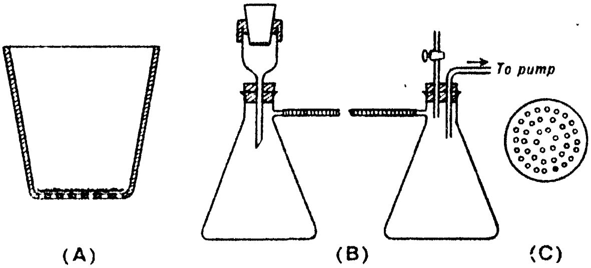

FIG. 2-31.

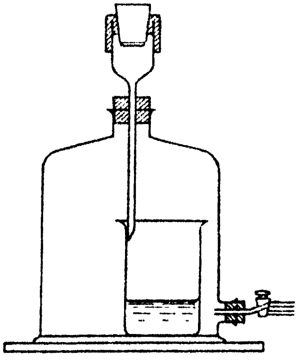

FIG. 2-32.

The Gooch crucible should be of suitable size. One about 4 cm. in height, with a capacity of 25 ml., and perforations about 0·5 to 0·8 mm. in diameter will be found serviceable for most purposes. The crucible is first placed in the suction filtering apparatus, and then half to two-thirds filled with the suspension of asbestos in water. The whole is allowed to stand for 2 to 3 minutes in order to allow the larger particles to settle to the bottom, and then suction is applied gently. When the water has passed through, the pump is turned on full, and the mat sucked down tight. The final uniform pad of asbestos should have a thickness of 2 to 3 mm. (see Fig. 58, *A*) ; it is possible to tell approximately when the mat has the correct thickness by holding the crucible up to the light and looking through it, when the outline of the holes should be barely visible. If the pad is too thin, more asbestos must be added and the process repeated. The asbestos pad is now thoroughly washed with distilled water under the maximum suction of the pump until no fine fibres pass into the filtrate. It should be mentioned that some analysts prefer to place a perforated porcelain plate (" Witt " plate, Fig. 2-31, *C*) upon the asbestos mat to prevent its dislodgement : a little more of the suspension is poured in to furnish enough asbestos to barely cover the plate and to hold it in place. This procedure is unnecessary if it be remembered that no liquid may be poured into the crucible unless suction is being applied. Liquids should be poured gently on to the centre of the mat down a stirring rod : a jet of water from a wash bottle should never be directed into the prepared crucible. If these precautions are taken there is little danger that the mat will become torn and allow the precipitate to pass through.

The crucible is placed on a small ignition dish or saucer or upon a shallow-form vitreosil capsule and dried to constant weight at the same temperature as that which will be subsequently used in drying the precipitate. For temperatures up to about 250°C, a thermostatically controlled electric oven should be used. For higher temperatures, or if the crucible requires ignition, the crucible may be heated in an electrically-heated muffle furnace. If the latter is not available, it may be placed inside a larger nickel crucible fitted with an asbestos ring (as in Fig. **2-33**), and the larger crucible heated directly with a flame. In all cases the crucible is allowed to cool in a desiccator (Section **II**, **10N**) before weighing.

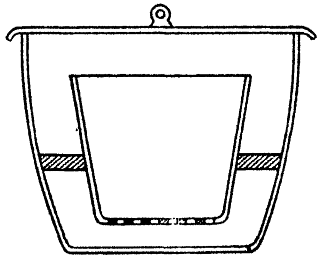

FIG. 2-33.

Attention is directed to **vitreosil Gooch crucibles,** which are obtainable in both translucent and transparent forms. These are more expensive than the ordinary porcelain crucibles, but they possess many obvious advantages. They can be heated to a much higher temperature without fear of cracking, and are generally more resistant to chemical reagents, particularly acids. If placed on a shallow vitreosil capsule, they may be ignited directly over a flame.

II, 32. Munroe crucibles.—A platinum Gooch crucible, containing a platinum mat, was devised by C. E. Munroe in 1888. The platinum mat is prepared by igniting a layer of ammonium chloroplatinate, moistened with alcohol, in the crucible. The chief features of such crucibles are: resistance to chemical attack, rapidity of filtration, retention of the finest precipitates, and possibility of heating to very high temperatures. The platinum mat lasts almost indefinitely, for the residues can be removed by any solution treatment which does not dissolve platinum. On account of the high price of platinum, Munroe crucibles are rarely employed in routine analysis; they find some application for most exacting work, as in atomic weight determinations.

II, 33. Crucibles fitted with permanent porous plates.—These possess an advantage over Gooch crucibles in so far that no preparation of a filter mat is necessary. The best known are the **Jena sintered glass crucibles.** They are made of an excellent resistance glass (Jena Geraetglas 20, designated by the symbol "*G*") and have a porous disc of sintered, ground glass fused into the body of the crucible (Fig. 2-34). The fused-in fritted filter disc can be obtained in various degrees of porosity. Thus the average size of the pores for plates numbered 1, 2, 3, and 4 are 100–120μ, 40–50μ, 20–30μ, and 5–10μ respectively. No. 4 is suitable for very fine precipitates (such as barium sulphate) and No. 3 for precipitates of medium particle size. Two types of crucible find the widest application in quantitative analysis, the low wide form (designated by the number *10*: thus *10G3* would refer to such a crucible with porosity 3) and the higher or tall form (designated by the number *1*, *e.g.*, *1G4*). A crucible with a capacity of 30 ml. is satisfactory for most work.

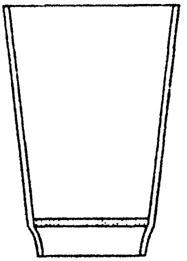

FIG. 2-34.

The advantages of Jena sintered glass crucibles are : (i) they are made entirely of glass, which is resistant to most chemical reagents with the exception of hydrofluoric acid and hot concentrated alkalis ; (ii) they can be dried to constant weight at 100°–150°C ; and (iii) they are readily cleaned. These crucibles can be heated to a temperature not exceeding 500°–550°C ; if heating above 150°C is required, they should be placed in a cold electric furnace, heated to the necessary temperature, and allowed to cool to about 200°C in the furnace before being removed to a desiccator.

For temperatures above 500°C, **Jena quartz filter crucibles** may be employed. These are similar to the Jena sintered glass crucibles, but are made of pure fused silica. They can be used up to 1300°C, and there is no danger of cracking through sudden changes of temperature. Two types are made, designated by the symbols *1bB3* and *4* and by *10B3* and *4*. They are attacked by phosphates and strong alkalis, but are otherwise very resistant to chemical reagents.

Another variety of crucible, which is likely to find wide application when its properties are better known, is the **porous porcelain filter crucible.** It consists of a porcelain crucible, glazed inside and outside, with a porous porcelain bottom ; the latter is available in a number of porosities. The crucible may be heated to bright redness in a furnace or it may be heated inside a larger metal crucible (Fig. 60) directly with a burner. Heating and cooling should be gradual in order to minimise the danger of cracking.

Crucibles fitted with permanent porous plates are cleaned by shaking out as much of the solid as possible, and then dissolving out the remainder of the solid with a suitable solvent. An alternative method is to suck water or some other liquid through from the reverse side. The process will be evident upon reference to Fig. 2-35.

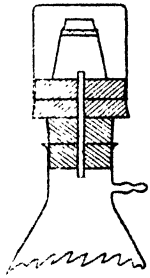

FIG. 2-35.

II, 34. Washing of precipitates.—Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile at the temperature at which the precipitate is ultimately dried, it is necessary to wash the precipitate to remove such material as completely as possible. The minimum volume of the washing liquid required to remove the objectionable matter should be used since no precipitate is absolutely insoluble. Qualitative tests for the removal of the impurities should be made on small volumes of the filtered washing solution. Furthermore, it is better to wash with a number of small portions of the washing liquid, which are well drained between each washing, than with one or two large portions, or by adding fresh portions of the washing liquid whilst solution still remains on the filter (see Section **I, 60**). The precipitate should never more than one-third to one-half fill the filter paper, and the liquid should be kept from 5 to 10 mm. below the edge.

The ideal washing liquid should comply as far as possible with the following conditions :

(1) it should have no solvent action upon the precipitate, and dissolve foreign substances easily ;

(2) it should have no dispersive action on the precipitate ;

(3) it should form no volatile or insoluble product with the precipitate ;

(4) it should be easily volatile at the temperature of drying of the precipitate ;

(5) it should contain no substance which is likely to interfere with subsequent determinations in the filtrate.

In general, water should not be used unless it is certain that it will not dissolve appreciable amounts of the precipitate or peptise it. If the precipitate is appreciably soluble in water, a common ion is usually added, since any electrolyte is less soluble in a dilute solution containing one of its ions than it is in pure water (Section **I, 9**) ; as an example the washing of calcium oxalate with dilute ammonium oxalate solution may be cited. If the precipitate tends to become colloidal and pass through the filter paper (this is frequently observed with gelatinous or flocculent precipitates), a wash solution containing an electrolyte must be employed (compare Section **I, 56**). The nature of the electrolyte is immaterial provided it has no action upon the precipitate during washing and is volatilised during the final heating. Ammonium salts are usually selected for this purpose : thus ammonium nitrate solution is employed for washing ferric hydroxide. In some cases it is possible to select a solution which will both reduce the solubility of the precipitate and prevent peptisation, for example, the use of dilute nitric acid with silver chloride. Some precipitates tend to oxidise during washing ; in such instances the precipitate cannot be allowed to run dry, and a special washing solution which reconverts the oxidised compounds into the original condition must be employed, *e.g.*, acidulated hydrogen sulphide water for copper sulphide. Gelatinous precipitates, like aluminium hydroxide, require more washing than crystalline ones, such as calcium oxalate. With gelatinous precipitates there is also a danger of channel formation if the wash liquid is allowed to drain completely ; these precipitates should be washed as far as possible by decantation.

The reader may have observed that full details of the technique of filtration have not so far been given. This is because the filtration of a precipitate is so closely associated with the washing process that a consideration of the former is logically deferred until the latter has been discussed, at least in outline.

II, 35. Technique of filtration.—When the proper filtering medium (filter paper, Gooch crucible, etc.) has been prepared, as much as possible of the supernatant liquid is poured off without disturbing the precipitate by directing the stream of liquid against a glass rod held against the lip of the beaker (compare Fig. 2-30). The precautions already mentioned against filling a filter paper too full must be taken. In most cases, particularly if the precipitate settles rapidly or is gelatinous, **washing by decantation** may be employed. Twenty to fifty ml. of a suitable wash liquid is added to the residue in the beaker, the solid stirred up and allowed to settle. If the solubility of the precipitate allows, the solution should be heated, since *inter alia* the rate of filtration will thus be increased. When the supernatant liquid is clear, as much as possible of the clear liquid is decanted through the filtering medium. This process is repeated three to five times (or as many times as is necessary) before the precipitate is transferred to the filter. The main bulk of the precipitate is first transferred by mixing with the wash solution and pouring off the suspension, the process being repeated until most of the solid has been removed from the beaker. The precipitate adhering to the sides and the bottom of the beaker is removed as follows. The beaker is grasped in the left hand and the stirring rod is held firmly against the top of the beaker with the index finger and should project 2 to 3 cm. beyond the lip ; the wash bottle is controlled by the right hand. The beaker is inclined and a stream of water (or wash liquid) is directed against the precipitate to dislodge it and wash it against the rod into the filter. The process is shown diagrammatically for a filter paper in Fig. 2-36. For some precipitates, where washing by decantation is inadmissible because of solubility influences, the *whole* of the precipitate must be transferred to the filter in this way. After the above treatment there will generally be small amounts of the precipitate adhering to the walls of the beaker. These are removed by rubbing with a "policeman" (Section **II, 10L**); when all the particles have been dislodged, the "policeman" is rinsed with the wash liquid, and the remaining precipitate transferred to the filter.

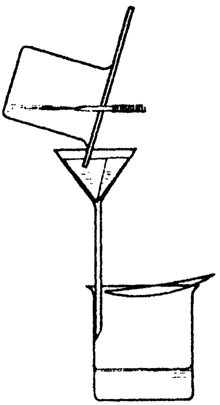
Fig. 2-36.

Where the precipitate is washed on the filter, in the last stages the washing solution is directed along the rim and then gradually towards the apex of the cone. In all cases, tests for the completeness of washing must be made by collecting a small sample of the washing solution after it is estimated that most of the impurities have been removed, and applying an appropriate qualitative test. Where filtration is carried out under suction, a small test tube may be attached to the bottom of the Gooch funnel by means of a wire.

II, 36. Drying and ignition of precipitates.—After a precipitate has been filtered and washed, it must be brought to a constant composition before it can be weighed. The further treatment will depend both upon the nature of the precipitate and upon that of the filtering medium. This treatment consists in drying or igniting the precipitate. Which of the latter two terms is employed depends upon the temperature at which the precipitate is heated. There is, however, no definite temperature below or above which the precipitate is said to be dried or ignited respectively. The meaning will be adequately conveyed for our purpose if we designate *drying* when the temperature is below 250°C (the maximum temperature which is readily reached in the usual thermostatically-controlled, electric drying oven), and *ignition* above 250°C up to, say, 1200°C. Precipitates that are to be dried should be collected on porcelain or silica Gooch, Jena sintered glass or porous porcelain filter crucibles. Precipitates that are to be ignited are collected on filter paper, porcelain, but preferably, silica Gooch crucibles, porous porcelain filter crucibles, Jena sintered glass crucibles (not above 550°C), Jena quartz filter crucibles, or, less commonly, in platinum Gooch crucibles. Ignition in crucibles containing either asbestos or a sintered glass disc as the filtering medium is simply effected by placing in a larger nickel or platinum crucible, as in Fig. 2-33, and heating with the appropriate burner (Section **II, 10A**) ; alternatively, these crucibles (and, indeed, any type of crucible) may be placed in an electrically-heated muffle furnace, which is equipped with a pyrometer and a means for controlling the temperature.

Many of the precipitates which are subsequently to be ignited are filtered through filter paper, and it is therefore necessary to describe the method to be adopted in such cases. The exact technique will depend upon whether the precipitate may be safely ignited in contact with the filter paper or not. It must be remembered that some precipitates, such as barium sulphate, may be reduced or changed in contact with filter paper or its decomposition products.

A. Incineration of the filter paper in the presence of the precipitate. On account of cheapness, porcelain crucibles are usually employed for this operation, particularly in instructional courses. Silica crucibles, although somewhat more expensive, are to be preferred because of their greater resistance to thermal shock. The crucible is first ignited to constant weight (*i.e.*, to within 0·0002 g.) at the same temperature as that to which the precipitate is ultimately heated. The well-drained filter paper and precipitate are carefully detached from the funnel ; the filter paper is folded so as to completely enclose the precipitate, care being taken not to tear the paper.* The packet is then placed point down in the weighed crucible, which is supported on a pipe-clay or, better, a silica triangle resting on a ring stand as in Fig. 2-37.† The crucible is slightly inclined, as shown in the diagram, and covered partially with the lid, which should rest partly on the triangle. A *very*

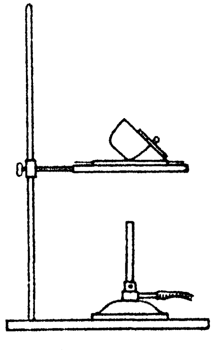

FIG. 2-37.

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* For bulky precipitates, such as those containing macerated filter paper, it is advisable to remove most of the moisture by a preliminary drying in the steam oven, or at 100–105°C.

† It is preferable to attach the triangle to the ring of a retort stand by bending the wire ends of the triangle round it rather than to support it on a tripod. In the former case, the crucible is more readily accessible and also the height of the crucible above the burner can be easily adjusted.

small flame is then placed under the crucible lid ; drying thus proceeds quickly and without undue risk. When the moisture has been expelled, the flame is increased slightly so as to *slowly* carbonise the paper. The paper should not be allowed to inflame as this may cause a mechanical expulsion of fine particles of the precipitate owing to the rapid escape of the products of combustion ; if, by chance, it does catch fire, the flame should be extinguished by momentarily placing the cover on the mouth of the crucible with the aid of a pair of crucible tongs. When the paper has completely carbonised and vapours are no longer evolved, the flame is moved to the back (bottom) of the crucible and the carbon slowly burned off whilst the flame is slowly increased.* After all the carbon has been burned away, the crucible is covered completely (if desired, the crucible may be placed in a vertical position for this purpose) and heated to the required temperature by means of a Bunsen, Méker or Fisher flame. Usually it takes about 20 minutes to char the paper, and 30 to 60 minutes to complete the ignition.

When the ignition is ended, the flame is removed and, after 1 to 2 minutes, the crucible and lid are placed in a desiccator containing a suitable desiccant (Section **II, 10 N**), and allowed to cool for 25 to 30 minutes. The crucible and lid are then weighed. The crucible and contents are then ignited at the same temperature for 10 to 20 minutes, allowed to cool in a desiccator as before, and weighed again. The ignition is repeated until constant weight is attained. Crucibles should always be handled with clean crucible tongs.

B. Use of crucible with interior-fitting serrated lid. J. D. Main Smith (1925) has designed an improved form of crucible lid. This is an interior-fitting lid of which the vertical flange is serrated around the edge ; it fits into a squat-shaped crucible, the upper surface of the lid being about 1 cm. from the top of the crucible (Fig. 2-38). The advantages are : (i) gases or vapours, which are disengaged in the operation, can escape freely ; (ii) loss by creeping, spattering and decrepitation are prevented ; (iii) the contents of the crucible can be easily inspected, since the lid easily swivels up by pressing on

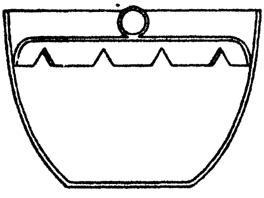
FIG. 2-38.

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* If the carbon on the lid is oxidised only slowly, the cover may be heated separately in a flame. It is of course held in clean crucible tongs.

one side lightly with the clean crucible tongs (this is, of course, unnecessary if the lid is of transparent silica) ; (iv) liquids can easily be added simply by pouring on to the lid, the serrations providing ingress into the crucible. Vitreosil crucibles of 15, 25, 40, and 50 ml. capacity with serrated lids are commercially available, and are comparatively inexpensive. Lids of transparent silica can also be obtained.

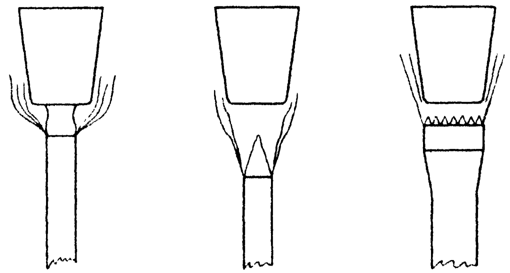
The ignition of a precipitate in a wet filter paper is readily effected by placing the precipitate and filter into a previously ignited and weighed crucible and lid, and conducting the initial heating exactly as described under **A.** Care must be taken that a sufficiently large crucible is used (usually of 40 ml. capacity) ; an over-large crucible is no disadvantage. After the paper has been carbonised and vapours are no longer evolved, the lid is removed and laid aside upside-down on a clock glass, and the combustion of the carbon completed at a red heat in the usual manner. If the lid has been blackened by the preliminary heating, it should be held by the ring upside-down by means of clean crucible tongs, and carefully ignited over the open crucible by means of a small flame until all the carbon has been burned off ; the clean lid is then replaced in the crucible, care being taken that any fragments of residue present fall into the crucible. The crucible and lid are then ignited at the appropriate temperature to constant weight.

C. Incineration of the filter paper apart from the precipitate. This method is employed in all those cases where the ignited substance is reduced by the burning paper, for example, barium sulphate, lead sulphate, bismuth oxide, copper oxide, etc. The funnel containing the precipitate is covered by a piece of qualitative filter paper upon which is written the formula of the precipitate and the name of the owner ; the paper is made secure by crumpling its edges over the rim of the funnel so that they will engage the outer conical portion of the funnel. The funnel is placed in the steam oven, or in a drying oven maintained at 100° to 105° C, for 1 to 2 hours or until completely dry. A sheet of glazed paper about 25 cm. square (white or black, to contrast with the colour of the precipitate) is placed on the bench away from all draughts. The dried filter is removed from the funnel, and as much as possible of the precipitate is removed from the paper and allowed to drop on a clock glass resting upon the glazed paper. This is readily done by very gently rubbing the sides of the filter paper together, when the bulk of the precipitate becomes detached and drops upon the clock glass. Any small particles of the precipitate which may have fallen upon the glazed paper are brushed into the crucible with a small camel-hair brush. The clock glass containing the precipitate is then covered with a larger clock glass or with a beaker. The filter paper is now carefully folded and placed inside a weighed porcelain or silica crucible. The crucible is placed on a triangle and the filter paper incinerated as detailed in the first paragraph of this Section. The crucible is allowed to cool, and the filter ash subjected to a suitable chemical treatment in order to convert any reduced or changed material into the form finally desired. The cold crucible is then placed upon the glazed paper and the main part of the precipitate carefully transferred from the clock glass to the crucible. A small camel-hair brush will assist in the transfer. Finally, the precipitate is brought to constant weight by heating to the necessary temperature.

Here also the Main Smith crucible may be used. The dried filter paper, from which most of the precipitate has been detached as described above, is first ignited exactly as already detailed. The crucible and lid are allowed to cool, a small quantity of the liquid chemical required to convert any reduced or changed material to the form finally desired is poured on to the lid, and the whole slowly heated to the correct temperature. The crucible is then allowed to cool, placed upon a sheet of glazed paper, the main part of the precipitate added, and the whole ignited to constant weight at the appropriate temperature.

II, 37. The care and use of platinum vessels.—Platinum has a very high melting point (1770°C). The pure metal is, however, too soft for general use, and is therefore always hardened with small quantities of rhodium, iridium, or gold. These alloys are slightly volatile at temperatures above 1100°C, but retain most of the advantageous properties of pure platinum, such as resistance to most chemical reagents including molten alkali carbonates and hydrofluoric acid (the exceptions are dealt with below), excellent conductivity of heat, and extremely small adsorption of water vapour. If the financial resources of the laboratory are limited, at least two crucibles of 25 ml. capacity, provided with covers, should be purchased ; these will meet most ordinary requirements. It is useful, if finances permit, to have crucibles of 10 ml. capacity and platinum dishes of 100, 300 and 500 ml. capacity.

Platinum crucibles should be supported when heated upon a platinum triangle. If the latter is not available, a silica or pipe-clay triangle may be used ; nichrome and other metal triangles should be avoided. Hot platinum crucibles must always be handled with platinum-tipped crucible tongs, or with ordinary tongs which are covered with platinum foil, securely attached by platinum wire. Unprotected brass or iron tongs produce stains on the crucible. Vessels of platinum must not be exposed to a luminous flame, nor may they be allowed to come into contact with the inner cone of a gas flame (see Fig. 2-39) ; this may result in the disintegration of the surface of the metal, causing it to become brittle, owing, probably, to the formation of a carbide of platinum.



Incorrect position *Correct position*
Bunsen flame
Correct position
Méker or Fisher flame

FIG. 2-39.

Platinum apparatus may be used without sensible loss for* :

1. Fusions with (*a*) sodium carbonate or fusion mixture, (*b*) borax, (*c*) alkali bifluorides, and (*d*) alkali bisulphates (slight attack in the last case above 700°C, which is diminished by the addition of ammonium sulphate).

2. Evaporations with (*a*) hydrofluoric acid, (*b*) hydrochloric acid in the absence of oxidising agents which yield nascent chlorine, and (*c*) concentrated sulphuric acid (a slight attack may occur).

3. Ignition of (*a*) barium sulphate and sulphates of metals which are not readily reducible, (*b*) alkaline earth carbonates, oxalates, etc., and (*c*) oxides which are not readily reducible, *e.g.*, CaO, SrO, BaO, Al_2O_3, Cr_2O_3, Mn_3O_4, TiO_2, ZrO_2, ThO_2, MoO_3, and WO_3.

* Extracted from the booklet entitled *Platinum Laboratory Apparatus* issued by Johnson Matthey and Co. Ltd., Hatton Garden, London, E.C.1, England. Further details will be found in this booklet.

Platinum is attacked under the following conditions, and such operations must not be conducted in platinum vessels :

1. Heating with the following liquids : (*a*) aqua regia, (*b*) hydrochloric acid and oxidising agents, (*c*) liquid mixtures which evolve bromine or iodine, (*d*) concentrated sulphuric acid (slight action, which is, however, negligible for most purposes), and (*e*) concentrated phosphoric acid (slight, but appreciable action after prolonged heating).

2. Heating with the following solids, their fusions or vapours : (*a*) oxides, peroxides, hydroxides, nitrates, nitrites, sulphides, cyanides, ferricyanides and ferrocyanides of the alkali and alkaline earth metals, (*b*) molten lead, silver, copper, bismuth, tin or gold, or mixtures which form these metals upon reduction, (*c*) phosphorus, arsenic or antimony, or mixtures which form these elements on reduction, particularly phosphates in the presence of reducing agents, (*d*) sulphur (slight action), selenium, and tellurium, (*e*) volatile halides, especially those which readily decompose, and (*f*) substances of unknown composition.

Cleaning and preservation of platinum ware. All platinum apparatus (crucibles, dishes, etc.) should be kept clean, polished and in proper shape. If, say, a platinum crucible becomes stained, it should be fused with a little sodium carbonate, the molten solid poured out on to a dry stone or iron slab, the residual solid dissolved out with water, and the vessel then digested with concentrated hydrochloric acid : this treatment may be repeated, if necessary. If fusion with sodium carbonate is without effect, potassium hydrogen sulphate may be substituted ; a slight attack of the platinum will occur. In some cases, the use of hydrofluoric acid or potassium hydrogen fluoride may be necessary.

If the surface exhibits signs of becoming dull, the vessel must be polished with fine silver sand, say of 75 to 100 mesh. Care must be taken that the sand consists of rounded grains (examine under microscope) and that it is free from angular pieces and grit, which would scratch the metal. The sand should be moistened and applied with the finger or a soft cloth.

All platinum vessels must be handled with care to prevent deformation and denting. Platinum crucibles must on no account be squeezed with the object of loosening the solidified cake after a fusion. Boxwood formers can be purchased for crucibles and dishes; these are invaluable for reshaping dented or deformed platinum ware.

II, 38. Perforated screens for crucibles.—It is often important to exclude flame gases from the interior of a crucible during an ignition, *e.g.*, in the ignition of ferric oxide. For this purpose we may employ a vitreosil plate, about 10 cm. square, in which a round opening is cut large enough to admit the crucible to two-thirds of its depth. The plate is held at an angle of about 30° from the horizontal by means of a clamp; alternatively, but less satisfactorily, it may be suspended on a tripod. Asbestos board may also be employed, but this has the disadvantage that fibres may adhere to the crucible: this difficulty is less likely to occur with " uralite." To obtain the maximum temperature, the following device may be used. An asbestos, " uralite " or vitreosil sheet is provided with a comparatively large hole, say, 5 cm. in diameter; upon this is placed a thin sheet of platinum with an opening just large enough to support the crucible.

CHAPTER III

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

III, 1. Preparation of a standard acid. *Discussion.*—Two acids, namely, hydrochloric acid and sulphuric acid, are widely employed in the preparation of standard solutions of acids. Both of these are commercially available as concentrated solutions ; concentrated hydrochloric acid is about 10·5 to 12*N*, and concentrated sulphuric acid is about 36*N*. By suitable dilution, solutions of any desired *approximate* strength may be readily prepared. Hydrochloric acid is generally more convenient, since most chlorides are soluble in water. Sulphuric acid forms insoluble salts with lime and baryta ; for titration of hot liquids or for determinations which require boiling for some time with excess of acid, standard sulphuric acid is, however, preferable. Nitric acid is rarely employed, because it almost invariably contains a little nitrous acid, which has a destructive action upon many indicators.

For the present, we shall confine our attention to the preparation of standard solutions of hydrochloric acid Two methods are available. The first utilises the experimental fact that aqueous solutions of hydrochloric acid lose either hydrogen chloride or water upon boiling, according as to whether they are stronger or weaker, until they attain a practically constant composition (constant boiling point mixture), which depends upon the prevailing pressure. The composition of this constant boiling mixture and its dependence upon pressure has been determined with great accuracy by Hulett and Bonner (1909) and by Foulk and Hollingsworth (1923). The relevant data are collected in Table XXX. The constant boiling point acid is neither hygroscopic nor appreciably volatile, and its concentration remains unchanged if kept in a well-stoppered vessel out of direct sunlight. This acid may be employed directly in the preparation of a solution of hydrochloric acid of known concentration.

In the second method a solution of the approximate strength required is prepared, and this is standardised against some standard alkaline substance, such as borax or anhydrous

TABLE XXX. COMPOSITION OF CONSTANT BOILING POINT HYDROCHLORIC ACID

Pressure (mm. of Hg)	*Per cent HCl in Acid (vac. wt.)*	*Grams of Acid, weighed in air, containing* 36·47 *g. of HCl.*
780	20·173	180·621
770	20·197	180·407
760	20·221	180·193
750	20·245	179·979
740	20·269	179·766
730	20·293	179·555

sodium carbonate ; other suitable substances are given in Section **III, 7**. Both methods will be described. If a solution of an exact normality is required, a solution of an approximate strength somewhat greater than that desired is first prepared ; this is suitably diluted with water after standardisation (for a typical calculation, see Section **I, 24**, Example *15*).

The student should read the following theoretical sections before embarking upon the experimental work :

Sections **I, 27** to **I, 29**—theory of acidimetry and alkalimetry ;

Section **I, 23**—equivalent weights, normal solutions.

III, 2. Preparation of constant boiling point hydrochloric acid.—*Method A* (J. A. Shaw, 1926). Mix 500 ml. of pure concentrated hydrochloric acid (sp. gr. 1·19), preferably of analytical reagent quality, with 500 ml. of distilled water* ; the resultant acid should have a specific gravity of 1·10 (test with a hydrometer). Fit up an apparatus consisting of a 1·5 litre Pyrex distilling flask surmounted with a splash bulb but no trap (which might set up a back pressure), and connected to a Liebig's condenser having a 75 cm. water jacket and an inner tube of 6 to 10 mm. bore. Insert the end of the condenser inside the neck of a Pyrex Erlenmeyer (conical) flask. Make all connexions with new rubber stoppers, and arrange that the glass tubing projects at least 2 cm. beyond the rubber. Place the diluted acid in the flask. To prevent superheating, allow the flask to rest on a sheet of asbestos in which a hole is cut for the flame ; insulate the upper part of the flask against heat radiation by means of asbestos paper or cloth. Conduct the distillation *continuously* at a rate not exceeding 8 to 10 ml. per minute. Do not immerse the condenser tip in the distillate, but allow the condensate to flow freely into the flask. Set aside the first 75 per cent of the volume of the original distillate for ordinary laboratory use, and retain the next 10 to 15 per cent as constant boiling point acid. Discard the residue in the flask (about 100 ml.). Read the barometric pressure to the nearest mm. at the beginning of the distillation, again after 75 per cent has passed over, and finally at the end of the distillation. The mean of the last two readings is calculated and the concentration of the acid interpolated from Table XXX.

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* If the concentrated acid has a specific gravity of 1·16, as is often the case, 300 ml. of water are required for 500 ml. of acid.

Method B. Mix 400 ml. of pure concentrated hydrochloric acid with 250 to 400 ml. of distilled water so that the specific gravity of the resultant acid is 1·10 (test with a hydrometer). Insert a thermometer in the neck of a 1 litre Pyrex distilling flask so that the bulb is just opposite the side tube, and attach a Liebig's condenser to the side tube ; use new rubber bungs. Place 500 ml. of the diluted acid in the flask and distil the liquid at a rate not exceeding 8 to 10 ml. per minute (3 to 4 ml. per minute is a convenient rate), and collect the distillate in a small Pyrex flask. From time to time pour off the distillate into a 500 ml. measuring cylinder. When 375 ml. has been collected and transferred to the measuring cylinder, collect a further 50 ml. in the small Pyrex flask ; watch the thermometer to see that the temperature remains constant. Remove the receiver and cork it. This contains the pure constant boiling point acid. Note the barometric pressure to the nearest mm. during the distillation and at the end, and take the mean value. Interpolate the concentration of the acid from Table XXX.

III, 3. Direct preparation of 0·1N hydrochloric acid from the constant boiling point acid.—Weigh a small, dry conical flask, fitted with a cork. Add the calculated quantity of constant boiling point acid required for the preparation of 1 litre of 0·1N acid (see Table XXX) with the aid of a pipette ; make the final adjustment with a small piece of glass capillary, to one end of which a piece of rubber tubing is attached. By this method it should be possible to weigh the acid to the nearest centigram. Reweigh the flask to 0·001 g. after replacing the stopper. Add an equal volume of water to prevent loss of acid, and transfer the contents to a litre volumetric flask. Wash out the weighing flask several times with distilled water and add the washings to the original solution. Make up to the mark with distilled water. Insert the stopper and mix the solution thoroughly by shaking and inverting the flask repeatedly.

Note.—Unless a solution of exact normality is required, it is not necessary to weigh out the exact quantity of constant boiling acid. The exact normality may be calculated from the weight of acid used. Thus, if 18·305 g. of acid, prepared at 760 mm., was diluted to 1 litre, its normality would be 18·305/180·193 = 0·10118*N*.

Solutions of other concentrations are similarly prepared.

III, 4. Preparation of 0·1*N* hydrochloric acid and standardisation.—Measure out by means of a graduated cylinder or a burette 9 ml. of pure concentrated hydrochloric acid ; pour the acid into a litre volumetric flask or into a litre measuring cylinder (Fig. 2-24*B*) containing about 500 ml. of distilled water. Make up to the litre mark with distilled water and thoroughly mix by shaking. This will give a solution approximately 0·1*N* (1).

Note. 1. If 1*N* hydrochloric acid is required, use 90 ml. of the concentrated acid. If 0·01*N* acid is required, dilute two 50 ml. portions of the approximately 0·1*N* acid, removed with a 50 ml. pipette, in a volumetric flask to 1 litre.

Approximately 0·1*N* sulphuric acid is similarly prepared from 3 ml. of pure concentrated sulphuric acid.

Two excellent methods are available for standardisation. The first has been widely employed, but the second, of more recent date, is more convenient, less time-consuming, and equally accurate.

A. Standardisation with anhydrous sodium carbonate.

*Pure sodium carbonate.*Analytical reagent quality* sodium carbonate of 99·9 per cent purity is obtainable commercially. This contains a little moisture and must be dehydrated by heating at 260° to 270°C for half an hour and allowed to cool in a desiccator before use. Alternatively, pure sodium carbonate may be prepared by heating A.R. sodium bicarbonate to 260° to 270°C for 60 to 90 minutes ; the temperature must not be allowed to exceed 270°C, for above this temperature the sodium carbonate may lose carbon dioxide. A small quantity (5 to 10 g.) of A.R. sodium bicarbonate is placed in a porcelain, nickel or, best, a platinum crucible, and pressed against the walls of the crucible so as to form a uniformly thick layer. The crucible is heated by any of the following methods:

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* Analytical reagent will be abbreviated to A.R.

(i) Embed the crucible in a sand bath, immerse the bulb of a 360°C thermometer in the sand adjacent to the crucible, and heat the sand bath with a free flame; maintain the temperature at 260° to 270°C for one hour.

(ii) Use an air bath as in Fig. 2-13 or Fig. 2-33.

(iii) Heat in an electric furnace maintained at 265°C.

It is advisable to stir the mass occasionally. In all cases the crucible is allowed to cool in a desiccator, and, before it is quite cold, it is transferred to a warm, dry, glass-stoppered tube or bottle, out of which, when cold, it may be weighed rapidly as required. It is important to remember that anhydrous sodium carbonate is hygroscopic and exhibits a tendency to pass into the monohydrate.

Procedure. Weigh out accurately from a weighing bottle about 0·2 g. of the pure sodium carbonate into a 250 ml. conical flask (1), dissolve it in 50 to 75 ml. of water, and add 2 drops of methyl orange indicator (2) or preferably of methyl orange—indigo carmine indicator (Section **I, 29**), which gives a very much more satisfactory end point.* Rinse a clean burette three times with 5 ml. portions of the acid; fill the burette to a point 2 to 3 cm. above the zero mark and open the stop-cock momentarily in order to fill the jet with liquid. Examine the jet to see that no air bubbles are enclosed. If there are, more liquid must be run out until the jet is completely filled. Refill, if necessary, to bring the level above the zero mark; then slowly run out the liquid until the level is between the 0·0 and 0·5 ml. mark. Read the position of the meniscus to 0·01 ml. (Section **II, 22**). Place the conical flask containing the sodium carbonate solution upon a piece of unglazed white paper beneath the burette, and run in the acid slowly from the burette. During the addition of the acid, the flask must be constantly rotated with one hand whilst the other hand controls the stop-cock. Continue the addition until the methyl orange becomes a very faint yellow, or the green colour commences to become paler when the methyl orange—indigo carmine indicator is used. Wash the walls of the flask down with a little distilled water from a wash bottle, and continue the titration very carefully by adding the acid dropwise until the colour of the methyl orange becomes orange or a faint pink, or the colour of the mixed indicator is a neutral grey ; if the end point is overstepped with the latter indicator, the colour is magenta. This marks the end point of the titration, and the burette reading should be taken and recorded in a note book. The procedure is repeated with two or three other portions of sodium carbonate. The first (or preliminary) titration will indicate the location of the true end point within 0·5 ml. With experience and care, subsequent titrations can be carried out very accurately and should yield concordant results. From the weights of sodium carbonate and the volumes of hydrochloric acid employed, the strength of the acid may be computed for each titration. The arithmetical mean is taken as the strength of the solution.

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* This indicator is prepared by dissolving 1 g. of methyl orange and 2·5 g. of *purified* indigo carmine in 1 litre of distilled water, and filtering the solution. The colour change on passing from alkaline to acid solution is from green to magenta with a neutral grey colour at *p*H of about 4.

Notes. 1. For *elementary students*, an approximately 0·1*N* solution of sodium carbonate may be prepared by weighing out accurately about 1·3 g. of pure sodium carbonate in a weighing bottle or in a small beaker, transferring it to a 250 ml. volumetric flask, dissolving it in water (Section **II, 6, A** (iii)), and making up to the mark. The flask is well shaken. 25 Ml. portions are withdrawn with a pipette and titrated against the acid as described above. Individual titrations should not differ by more than 0·1 ml.
2. Alternatively, bromo-phenol blue or methyl yellow may be used as indicators. With the former a few drops of indicator solution impart a blue colour to the solution, which becomes purplish-green at the end point ; with the latter the colour changes are similar to those for methyl orange, but are more readily perceived.

Calculation of normality. The normality may be computed from the equation :

$$\mathrm{Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O},$$

but the best method is to derive the normality entirely in terms of the primary standard substance, here, sodium carbonate. The equivalent weight (Section **I, 23**) of sodium carbonate is 52·997 or 53·00. If the weight of the sodium carbonate is divided by the number of ml. of hydrochloric acid to which it is equivalent, as found by titration, we have the weight of primary standard equivalent to 1 ml. of the acid. Thus if 0·2500 g. of sodium carbonate is required for the neutralisation of 45·00 ml. of hydrochloric acid, 1 ml. of the acid would be equivalent to 0·2500/45·00 = 0·05556 g. of sodium carbonate. The milli-equivalent weight or the weight in 1 ml. of *N* sodium carbonate solution is 0·05300 g.

Hence the normality of the acid is 0·05556/0·05300 = 0·1048*N*.

Another method is the following. 0·2500 G. of sodium carbonate requires 45·00 ml. of acid, hence 1 litre of acid is equivalent to 1000 × 0·2500/45·00 = 55·56 g. of sodium carbonate. But a litre of *N* acid is equivalent to 53·00 g. of sodium carbonate, hence the acid is 55·56/53·00 = 0·1048*N*.

In the method described in Note 1 above, the normality of the sodium carbonate is first computed from the weight of sodium carbonate used. The mode of calculation described in Section **I, 24** is employed. If V_A is the volume in ml. of the standard solution of normality n_A required to react completely with V_A ml. of the unknown solution of normality n_B, then

$$V_A \times n_A = V_B \times n_B,$$

from which the value of n_A is readily deduced. Thus if 1·3890 g. of anhydrous sodium carbonate is dissolved in 250 ml. of water, the normality of the sodium carbonate solution is 1·3890 × 4/53·00 = 0·1048*N*. If 25 ml. of the sodium carbonate solution exactly neutralise 25·45 ml. of the hydrochloric acid, then

$$25{\cdot}00 \times 0{\cdot}1048 = 25{\cdot}45 \times n_B,$$

or the acid is 0·1030*N*.

B. Standardisation against borax. The advantages of sodium tetraborate decahydrate are : (i) it has a large equivalent weight, 190·72 (that of anhydrous sodium carbonate is 53·00) ; (ii) it is easily and economically purified by recrystallisation ; (iii) heating to constant weight is not required ; (iv) it is practically non-hygroscopic ; and (v) a sharp end point can be obtained with methyl red at room temperatures since this indicator has no effect upon the very weak boric acid.

$$Na_2B_4O_7,10H_2O + 2HCl = 2NaCl + 4H_3BO_3 + 5H_2O.$$

Pure borax. A.R. Borax is recrystallised from distilled water ; 50 ml. of water is used for every 15 g. of borax. Care must be taken that the crystallisation does not take place above 55°C ; above this temperature there is a possibility of the formation of the pentahydrate since the transition temperature, decahydrate $\rightleftharpoons$ pentahydrate, is 61°C. The crystals are filtered at the pump (Section **II, 12**), washed twice with water, then twice with portions of 95 per cent alcohol, followed by two portions of ether. 5 Ml. portions of water, alcohol or ether are used for 10 g. of borax crystals.

Each washing must be followed by suction to remove the wash liquid. After washing with alcohol and ether, the borax is spread in a thin layer on a watch or clock glass and allowed to stand at room temperature for 12 to 18 hours. The borax is then dry and may be kept in a well-stoppered tube for 3 to 4 weeks without appreciable change. An alternative method of drying is to place the recrystallised product after having been washed twice with water in a desiccator over a solution saturated with respect to sugar (sucrose) *and* sodium chloride. The borax is dry after about 3 days, and may be kept indefinitely in the desiccator without change. The latter method is more time-consuming; the product is identical with that obtained by the alcohol-ether process.

Procedure. Weigh out accurately from a weighing bottle 0·4 to 0·5 g. of pure borax into a 250 ml. conical flask (1), dissolve it in about 50 ml. of water and add a few drops of methyl red (2). Titrate with the hydrochloric acid contained in a burette (for details, see under **A**) until the colour changes to pink (3). Repeat the titration with two other portions of borax. Calculate the strength of the hydrochloric acid from the weight of borax and the volume of acid used. The average deviation of these results should not exceed 1 to 2 parts per thousand. If it is greater, further titrations must be performed until the average deviation is within these limits. The arithmetical mean is taken as the concentration of the solution.

Notes. 1. For *elementary students*, an approximately 0·1N solution of borax may be prepared by weighing out accurately 4·7 to 4·8 g. of A.R. borax on a watch glass or in a small beaker, transferring it to a 250 ml. volumetric flask, dissolving it in water (Section **II, 6, A** (iii)), and making up to the mark. The contents of the flask are well mixed by shaking. 25 Ml. portions are withdrawn with a pipette and titrated against the acid as detailed under *Method* **A**. Individual titrations should not differ by more than 0·1 ml.

2. Methyl orange, methyl orange—indigo carmine or bromocresol green may also be used as indicators (compare Note 2 in *Method* **A**). If the comparison solution procedure is adopted (see Note 3), the mixed indicator should not be used.

3. For work of the highest precision a comparison solution or colour standard may be prepared for detecting the equivalence point. For 0·1N solutions, this is made by adding 5 drops of methyl red to a solution containing 1·0 g. of sodium chloride and 2·2 g. of boric acid in 500 ml. of water; the solution must be boiled to remove any carbon dioxide which may be present in the water. It is assumed that 20 ml. of wash water are used in the titration.

Calculation of the normality. This is carried out as described in *Method* **A.** The equivalent weight of borax is 190·72.

III, 5. Preparation of standard alkali.—*Discussion.* The hydroxides of sodium, potassium and barium are generally employed for the preparation of solutions of standard alkalis. They are strong bases and are readily soluble in water. Solutions made from ammonium hydroxide are undesirable, because they tend to lose ammonia, especially if the concentration exceeds $0{\cdot}5N$; moreover, it is a weak base and difficulties arise in titrations with weak acid (compare Section **I, 36**). Sodium hydroxide is most commonly used because of its cheapness. None of these solid hydroxides can be obtained pure, so that a standard solution cannot be prepared by dissolving a known weight in a definite volume of water. Both sodium and potassium hydroxides are extremely hygroscopic ; a certain amount of alkali carbonate and water are always present. Exact results cannot be obtained in the presence of carbonate with some indicators, and it is therefore necessary to discuss methods for the preparation of carbonate-free alkali solutions. For many purposes the A.R. sodium hydroxide (which contains 1 to 2 per cent of sodium carbonate) or the commercially available sodium hydroxide prepared from metallic sodium (sodium carbonate content < 1 per cent) is sufficiently pure.

To prepare carbonate-free sodium hydroxide solution one of several methods may be used :

(i) Rinse the sticks of A.R. quality, or those prepared from metallic sodium, rapidly with water ; this removes the carbonate from the surface. A solution prepared from the washed sticks is satisfactory for most purposes.

(ii) If a concentrated solution of sodium hydroxide (equal weights of solid and water) is prepared, covered and allowed to stand, the carbonate remains insoluble ; the clear supernatant liquid may be poured or siphoned off, and suitably diluted. (Potassium carbonate is too soluble in the concentrated alkali for this method to be applicable.)

(iii) Carbonate may be removed by the addition of a slight excess of a concentrated solution of barium chloride or of barium hydroxide, shaking well, and allowing the precipitate to settle. The amount of $Ba(OH)_2,8H_2O$ or of $BaCl_2,2H_2O$ required is 10 g. or 8 g. respectively for 100 g. of A.R. sodium hydroxide.

(iv) The best method, which yields a product completely free from carbonate ions, consists in the electrolysis of a saturated solution of A.R. sodium chloride with a mercury cathode and a platinum anode in the apparatus shown in Fig. 3-1. About 20 to 30 ml. of *redistilled* mercury are placed in a 250 ml. pear-shaped Pyrex separating funnel, over which is poured about 100 to 125 ml. of an almost saturated solution of A.R. sodium chloride. Two short lengths of platinum wire are sealed into Pyrex glass tubing, one of these dips into the mercury (cathode) and the other into the salt solution (anode). A little mercury is placed in the glass tubes and electrical contact is made by means of amalgamated copper wires dipping into the mercury in the tubes. Electrolysis is carried out using 6 to 8 volts and 0·5 to 1 ampère for several hours ; the funnel is shaken at intervals in order to break up the amalgam crystals that form on the surface of the mercury. The weight of the sodium dissolved in the amalgam may be roughly computed from the total current passed ; the current efficiency is 75 to 80 per cent. When sufficient amalgam has formed, the mercury is run into a Pyrex or, preferably, a Jena flask containing about 100 ml. of boiled-out distilled water and closed with a rubber bung carrying a soda lime guard tube. Decomposition of the amalgam is complete after several days : after 12 to 18 hours about 75 per cent of the amalgam is decomposed. Dilute solutions of sodium hydroxide are prepared by transferring the concentrated solution to the appropriate quantity of boiled-out (or conductivity) water, an atmosphere of nitrogen being maintained throughout. This method is rather time-consuming, and need only be used for work demanding the highest precision.

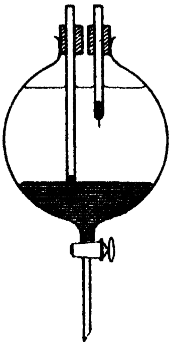

FIG. 3-1.

Attention must be directed to the fact that alkaline solutions, particularly if concentrated, attack glass. They may be preserved, if required, in either a paraffined bottle* or a bottle in which the inside is coated with a rubber paint, such as " Thermoprene " (compare Section **II, 25**).

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* The clean, dry bottle is warmed slightly and enough molten paraffin wax is poured in to give a thick coating. The bottle is rolled gently until an even thick coating is obtained and the paraffin wax is about to solidify. At this stage the bottle is stood upright so that an extra thick layer is formed at the bottom.

Furthermore, solutions of the strong bases absorb carbon dioxide from the air. If such solutions are exposed to the atmosphere for any appreciable time they become contaminated with carbonate. This may be prevented by the use of a storage vessel such as is shown in Figs. 2-25, 2-27 and 2-28; the guard tube should be filled with soda-lime or " sofnolite." A short exposure of an alkali hydroxide solution to the air will not, however, introduce any serious error. If such solutions are quickly transferred to a burette and the latter fitted with a soda-lime guard tube, the error due to contamination by carbon dioxide may be neglected.

The solution of alkali hydroxide prepared by any of the above methods must be standardised. Alkaline solutions that are subsequently to be used in the presence of carbon dioxide or with strong acids are best standardised against solutions prepared from constant boiling point hydrochloric acid or potassium bi-iodate or sulphamic acid, or against hydrochloric acid which has been standardised by means of borax or sodium carbonate. If the alkali solution is to be used in the titration of weak acids, it is best standardised against organic acids, such as benzoic acid or potassium hydrogen phthalate. The last two are commercially available in a purity exceeding 99·9 per cent. Potassium hydrogen phthalate is preferable, since it is more soluble in water and has a greater molecular weight.

Procedure A. Weigh out rapidly about 4·2 g. of A.R. sodium hydroxide on a watch glass or into a small beaker, dissolve it in water, make up to 1 litre with boiled-out distilled water, mix thoroughly by shaking, and pour the resultant solution into the stock bottle, which should be closed by a rubber stopper.

Procedure B (**carbonate-free sodium hydroxide**). Dissolve 50 g. of sodium hydroxide in 50 ml. of distilled water in a Pyrex or Jena flask, transfer to a 75 ml. test tube of Jena or Pyrex glass, and insert a well-fitting stopper covered with tin foil. Allow it to stand in a vertical position until the supernatant liquid is clear. For a 0·1*N* sodium hydroxide solution *carefully* withdraw 6·5 ml. of the concentrated clear solution through a graduated pipette (Fig. 2-18, *C*) into a litre bottle or flask, and dilute quickly with 1 litre of recently boiled-out water.

A clear solution can be obtained more quickly, and incidentally the transfer can be made more satisfactorily, by filtering the solution through a sintered glass funnel with exclusion of carbon dioxide with the aid of the apparatus shown in Fig. 3-2. It is advisable to roughly calibrate the test-tube in 5 ml. intervals and to put the graduations on a thin slip of paper gummed to the outside of the tube.

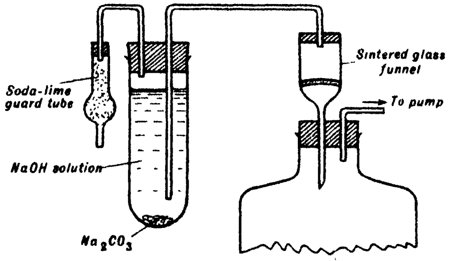

FIG. 3-2.

Procedure C (**carbonate-free sodium hydroxide.**) Weigh out about 5 g. of dry sodium hydroxide sticks or pellets on a watch glass on the rough balance, transfer to a 500 ml. Pyrex beaker, and dissolve in about 300 ml. of water. Warm and add slowly a solution (20 to 25 ml.) prepared from 2 to 2·5 g. of solid crystallised barium hydroxide or barium chloride. Allow the barium carbonate to settle, and decant the clear solution into a litre bottle or flask ; dilute to about 1 litre with carbon dioxide-free water and shake well. Allow the solution to settle again : siphon or filter off the solution into a clean bottle fitted with a rubber stopper. Alternatively, the solution may be stored in an apparatus similar to that shown in Figs. 2-25, 2-27 or 2-28 ; a soda-lime guard tube should be provided.

III, 6. Standardisation of the approximately 0·1*N* sodium hydroxide.—If the solution contains carbonate (*Procedure A*) methyl orange, methyl orange-indigo carmine, or bromophenol blue must be used in standardisation against hydrochloric acid of known normality. Phenolphthalein or indicators with a similar *p*H range, which are affected by carbon dioxide, cannot be used at the ordinary temperature (compare Section **I, 27**). With carbonate-free sodium hydroxide (*Procedure B*) phenolphthalein or thymol blue (Section **I, 33**) may be employed, and standardisation may be effected against hydrochloric acid, potassium bi-iodate, potassium hydrogen phthalate, benzoic acid, or other organic acids (Section **III, 7**).

Procedure A. **With standard hydrochloric acid.** Place the 0·1*N* hydrochloric acid, prepared from the constant boiling point acid or which has been standardised by means of sodium carbonate or borax, in the burette. Transfer 25 ml. of the sodium hydroxide solution into a 250 ml. conical flask with the aid of a pipette (1), dilute with a little water, add 1 to 2 drops of methyl orange or 3 to 4 drops of methyl orange-indigo carmine indicator, and titrate with the previously standardised hydrochloric acid. Repeat the titrations until duplicate determinations agree within 0·1 ml. of each other.

Note. 1. If another burette is available, the alkali solution may be placed in it, and definite volumes transferred from the burette to the conical flask for titrations. This method has the advantage that volumes of the order of 40 ml. of solution can be conveniently titrated, thus reducing the experimental error; also, back titration may be effected if the end point is overstepped.

Calculation of the normality. The normality is readily computed from the simple relationship

$$V_A \times n_A = V_B \times n_B,$$

where V_A and n_A refer to the volume and known normality of the acid respectively, V_B is the volume of alkali solution required for the neutralisation, and n_B is its (unknown) normality.

Procedure B. **With potassium hydrogen phthalate.** The A.R. potassium hydrogen phthalate has a purity of at least 99·9 per cent*; it is almost non-hygroscopic, but, unless a product of guaranteed purity is purchased, it is advisable to dry it at 120°C for 2 hours, and allow it to cool in a desiccator. Weigh out three 0·6 to 0·7 g. portions of the salt into 250 ml. Pyrex or Hysil conical flasks (1), add 75 ml. of boiled out water to each portion, stopper each flask and shake gently until the solid has dissolved. Titrate each solution with the sodium hydroxide solution contained in a burette, using phenolphthalein or thymol blue as indicator.

Calculation of normality. This is similar to that described in Section **III, 4.** The equivalent weight of potassium hydrogen phthalate is 204·22. The mean deviation should not exceed 0·1 to 0·2 per cent.

$$HK.C_8H_4O_4 + NaOH = NaK.C_8H_4O_4 + H_4O.$$

Note. 1. For *elementary students*, an approximately 0·1*N* solution is prepared by weighing out accurately about 5·1 g. of the ordinary A.R. product, dissolving it in water, and making it up to 250 ml. in a volumetric flask. 25 Ml. portions are employed in the titrations with the sodium hydroxide solution. Individual titrations should not differ by more than 0·1 ml. The normality is calculated in a similar manner to that given in Section **III, 4**; the equivalent weight is 204·22.

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* The U.S. Bureau of Standards supply a product of 99·97 per cent guaranteed purity. Products of 99·97 and 99·95 per cent purity can be obtained from the Eastman Kodak Co., U.S.A., and the Mallinckrodt Chemical Works, U.S.A., respectively. See Appendix, Section **A, 9.**

III, 7. Other standard substances for acidimetry and alkalimetry.—In addition to the standard substances already detailed for use in standardising acids and alkalis, numerous others have been proposed. A number of these will be briefly described.

A. Sodium oxalate ($Na_2C_2O_4$; equiv. wt. = 134·02). The A.R. product has a purity of 99·9 per cent. or better.* It is recommended that the salt be dried for 2 hours at 120°C before use in order to remove hygroscopic moisture. Upon strong heating the salt largely decomposes with the formation of sodium carbonate:

$$Na_2C_2O_4 = Na_2CO_3 + CO.$$

If a little carbon dioxide is lost by the decomposition of the sodium carbonate, no error is introduced because the total alkalinity is unaffected. Some of the salt (0·25 to 0·3 g. for a 0·1N solution) is carefully weighed into a platinum crucible, which is then covered with the lid. The crucible and lid are heated, while supported in a hole in a sheet of asbestos, over a small flame for 15 to 30 minutes until the sodium carbonate formed just begins to fuse. Towards the end of the operation the lid is moved aside to bring about the complete combustion of the carbon formed. The resultant carbonate is transferred to a conical flask or beaker, dissolved in water, and titrated against the acid solution, using methyl orange or methyl orange-indigo carmine as indicator. The disadvantages of the method are the possibility of mechanical loss during the evolution of carbon monoxide and its tedious nature.

B. Mercuric oxide (HgO; equiv. wt. = 108·31). Mercuric oxide can be readily obtained pure and dry, and has a comparatively high equivalent weight. It dissolves in potassium bromide solution with the production of potassium mercuric bromide and an equivalent quantity of potassium hydroxide:

$$HgO + 4KBr + H_2O = K_2[HgBr_4] + 2KOH.$$

A 0·1N solution of potassium hydroxide is obtained by dissolving 10·83 g. of A.R. mercuric oxide in a solution of 200

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* A guaranteed product of 99·95 per cent purity is supplied by the U.S. Bureau of Standards and also by the Mallinckrodt Chemical Works, U.S.A. (see Appendix Section **A, 9**).

g. of A.R. potassium bromide in 300 ml. of water, and diluting to 1 litre. This solution may be titrated against acids with *inter alia* phenolphthalein or methyl orange as indicators.

C. Benzoic acid ($H.C_7H_5O_2$; equiv. wt. = 122·12). The A.R. product has a purity of at least 99·9 per cent.* For work demanding the highest accuracy, the acid should be dried before use by careful fusion in a platinum crucible at about 130°C, and then powdered in an agate mortar. Benzoic acid is sparingly soluble in water (which is a disadvantage) and must therefore be dissolved in 95 per cent alcohol. The mode of use is similar to that already described for potassium hydrogen phthalate (Section **III, 6B**). For a $0{\cdot}1N$ solution, of, say, sodium hydroxide, weigh out accurately 0·4 g. portions of the acid into a 250 ml. conical flask, add 10 ml. of alcohol, shake until dissolved, and then titrate the solution against the strong alkali using phenolphthalein as indicator. A blank test should be made with the same volume of alcohol and the indicator : deduct, if necessary, the volume of the alkali solution consumed in the blank test.

D. Succinic acid ($H_2.C_4H_4O_4$; equiv. wt. = 59·045). The A.R. product or a pure commercial product should be recrystallised from pure acetone and dried in a vacuum desiccator. The purity is checked by means of a melting point determination (185°–185·5°C). The acid is fairly soluble in water ; phenolphthalein is a suitable indicator.

E. Furoic acid ($H.C_5H_3O_3$; equiv. wt. = 112·08). The purified commercial acid, m.p. 131°–132°C, is crystallised once from chloroform and dried at 120°C for 2 hours. The technical product is purified by one recrystallisation from hot water with the aid of a little animal charcoal (2 g. of animal charcoal for 20 g. of acid), dried at 120°C for 2 hours, and then recrystallised from chloroform as above. The resultant solid is pure. The acid is only moderately soluble in cold water, and is best dissolved in alcohol as detailed under **C** for benzoic acid. Phenolphthalein or an indicator of similar *p*H range must be used in the titration with a strong base.

F. Adipic acid ($H_2.C_6H_8O_4$; equiv. wt. = 73·07). The commercial acid is crystallised once from hot water with the addition of a little animal charcoal, dried at 120°C for 2 hours, then recrystallised from acetone and again dried at 120°C for 2 hours. The pure acid has a melting point of 152°C. The acid is slightly soluble in cold water, but, like furoic acid, it dissolves readily in hot water and can be titrated in hot solution with an indicator of the phenolphthalein type. It is best, however, to dissolve it in rectified spirit (compare benzoic acid above). This is an excellent and inexpensive standard.

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* A guaranteed product of 99·95 per cent. purity is supplied by the U.S. Bureau of Standards. An acid of similar purity can also be obtained from the Mallinckrodt Chemical Works, U.S.A. See Appendix, Sections **A, 8, 9.**

G. Potassium bi-iodate ($KH(IO_3)_2$; equiv. wt. = 389·95). Unlike the other solid standards already described, this is a strong acid and thus permits the use of any indicator having a *p*H range between *p*H 4·5 and 9·5 for titration with strong bases (compare Section **I, 38**). It may be employed for the standardisation of bases which are subsequently to be used with strong acids ; an indicator, such as methyl red, must then be used. The salt is fairly soluble in water, is anhydrous and non-hygroscopic, and the aqueous solutions are stable for long periods ; the equivalent weight is high. The only disadvantage is that the pure substance is expensive.* A 0·1*N* solution of potassium bi-iodate contains 38·995 g. per litre.

Preparation of pure potassium bi-iodate. 42 Grams of A.R. iodic acid are dissolved in 170 ml. of water, and half neutralised by the addition of potassium hydroxide solution prepared from A.R. caustic potash. The mixture is heated to boiling, six drops of concentrated hydrochloric acid added, and, after all has dissolved, the mixture is cooled. The separated potassium bi-iodate is filtered on a Jena sintered funnel, and purified by three crystallisations from hot water. The final product is dried at 100°C for several hours ; it is 99·97 per cent pure.

H. Oxalic acid dihydrate ($H_2.C_2O_4,2H_2O$; equiv. wt. = 63·034). The A.R. acid has been widely used as a standard, but in view of the possible uncertainty of the water content this is not recommended except for elementary students. The latter objection may be surmounted if the acid is preserved in a desiccator over deliquescent sodium bromide.

I. Potassium tetroxalate ($KHC_2O_4,H_2C_2O_4,2H_2O$; equiv. wt. = 84·732). This is suitable only for elementary or approximate work owing to the possible uncertainty of the water content.

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* A very pure product, prepared from iodic acid of electrolytic origin, is made by the G. F. Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio, U.S.A. The agents for Great Britain are F. W. Berk and Co. Ltd., 52-54 Leadenhall Street, London, E.C.3, England.

J. Potassium bi-tartrate ($KHC_4H_4O_6$; equiv. wt. = 188·18). The A.R. product has a purity of 99·9 per cent. The substance is sparingly soluble in cold water and must be titrated in hot solution, in which it is more soluble.

Phenolphthalein or thymol blue must be used as indicators for **H, I** and **J.**

K. Sulphamic acid (NH_2SO_2OH ; equiv. = 97·09). A product of comparatively high purity has recently become commercially available.* It is prepared by the action fo fuming sulphuric acid upon urea :

$$CO(NH_2)_2 + H_2SO_4 + SO_3 = 2NH_2SO_2OH + CO_2.$$

It is purified by crystallisation from hot water (see below). The acid is moderately soluble in water (21·3 g. and 47·1 g. in 100 g. of water at 20°C and 80°C respectively), appreciably soluble in methanol and ethanol, slightly soluble in acetone, and practically insoluble in ether ; it is a colourless, crystalline, non-hygroscopic solid melting with decomposition at 205°C. Sulphamic acid is largely dissociated in aqueous solution (it is similar to hydrochloric acid in this respect), so that any indicator with a *p*H range of 4 to 9 may be employed with the $0 \cdot 1N$ solution ; the best indicator for use with strong bases is bromo-thymol blue. The substance may be employed as a primary standard, and, for general use, is probably preferable to the expensive potassium bi-iodate. The aqueous solution is, however, not stable, as hydrolysis *slowly* occurs at room temperature with the formation of ammonium bisulphate :

$$NH_2SO_2OH + H_2O = NH_4HSO_4.$$

Purification of sulphamic acid (G. F. Smith, 1938). Dissolve 125 g. of the commercial product in 300 ml. of water preheated to 70°C. Filter the hot solution three times and discard each time the material crystallising from solution (altogether about 25 g.) ; there will, of necessity, be a lowering of temperature during this process. Cool the final filtrate in a mixture of ice and salt for 20 minutes, filter on a sintered glass funnel, and wash successively with a small quantity of ice water, twice with cold ethyl alcohol, and anhydrous ether. Dry the recrystallised solid in the air for 1 hour, grind it in an agate or glass mortar, and preserve in a desiccator. The resultant sulphamic acid is 99·95 per cent pure. The substance may also be dried at 105°C ; decomposition commences at about 135°C.

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* From the Eastman Kodak Co., Rochester, N.Y., U.S.A.

III, 8. Standard barium hydroxide (baryta) solution.—This solution is widely employed, particularly for the titration of organic acids. Barium carbonate is insoluble, so that a clear solution is a carbonate-free strong alkali. The equivalent weight of $Ba(OH)_2,8H_2O$ is 167·75, but a standard solution cannot be prepared by direct weighing owing to the uncertainty of the hydration and the possible presence of carbonate. To prepare an approximately 0·1*N* solution, dissolve 18 g. of A.R. crystallised baryta (or 20 g. of the commercial substance) in about 1 litre of water in a large flask. Stopper the flask and shake until all the crystals have disappeared. Allow the solution to stand for 2 days or until all the barium carbonate has completely settled out. Decant or siphon off the clear solution into a storage bottle of the type depicted in Figs. 2-25, 2-27 or 2-28. A soda-lime guard tube must be provided to prevent ingress of carbon dioxide. The solution may be standardised against standard 0·1*N* hydrochloric acid or potassium hydrogen phthalate ; phenolphthalein or thymol blue is employed as indicator.

ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI

III, 9. Determination of the Na_2CO_3 content of washing soda. *Procedure.* Weigh out accurately about 3·6 g. of the washing soda crystals, dissolve in water, and make up to 250 ml. in a graduated flask. Mix thoroughly. Titrate 25 ml. of the solution with standard hydrochloric acid of approximately 0·1*N* concentration using methyl orange, or, better, methyl orange-indigo carmine or bromo-cresol green as indicator (compare Table X). Two consecutive titrations should agree within 0·1 ml.

Calculation. The weight of anhydrous sodium carbonate Na_2CO_3 which has reacted with the standard hydrochloric acid can be readily computed from the equation :

$$\underset{106{\cdot}01}{Na_2CO_3} + \underset{2 \times 35{\cdot}46}{2HCl} = 2NaCl + H_2O + CO_2$$

The percentage of Na_2CO_3 can then be calculated from the known weight of washing soda employed.

A simpler and more general procedure is to employ the " normality " method. A normal solution of sodium carbonate contains 53·00 g. of Na_2CO_3 per litre ; 1 ml. of a *N* solution of sodium carbonate contains 0·05300 g., or the milliequivalent weight. If the volume of hydrochloric acid be multiplied by the normality we obtain the number of ml. of *N* acid. By multiplying the latter figure by the milli-equivalent weight of sodium carbonate, the weight of Na_2CO_3 in the sample titrated is found: 1 ml. *N* HCl = 0·05300 g. of Na_2CO_3. The percentage of Na_2CO_3 can then be readily calculated.

An actual example will make this clear.

Weight of weighing bottle + substance	= 16·7910 g.
Weight of weighing bottle + residual substance	= 13·0110 g.
∴ Weight of sample used	= 3·7800 g.

This was dissolved in water and made up to 250 ml.

Titration of 25·0 ml. of the carbonate solution against 0·1060*N* HCl, with methyl orange-indigo carmine as indicator.

Experiment	*Reading* 1	*Reading* 2	*Difference*
1	0·00 ml.	26·10 ml.	26·10 ml. (preliminary)
2	0·00 ml.	25·90 ml.	25·90 ml.
3	0·00 ml.	25·95 ml.	25·95 ml.
		Mean	25·93 ml.

1 Ml. *N* HCl ≡ 0·05300 g. Na_2CO_3.

25·93 × 0·1060 ≡ 2·749 ml. *N* HCl.

2·749 × 0·05300 = 0·1457 g. Na_2CO_3 in portion titrated.

Weight of washing soda in portion titrated
= 3·7800 × 25·0/250 = 0·3780 g.

∴ Percentage of Na_2CO_3 = 0·1457 × 100/0·3780 = *38·54%*

Alternative method of calculation.

25·0 Ml. of the carbonate solution required 25·93 ml. of 0·1060*N* HCl;

∴ 25·0 × normality of carbonate solution = 25·93 × 0·1060, whence the carbonate solution is 25·93 × 0·1060/25·0 = 0·1099*N*. But *N* Na_2CO_3 contains 106·00/2 = 53·00 g. Na_2CO_3 per litre,

∴ the given solution contains 0·1099 × 53·00 = 5·8271 g. Na_2CO_3 per litre, and 250 ml. would contain 5·8271 × 250/1000 = 1·4568 g.

Thus percentage of Na_2CO_3 = 1·4568 × 100/3·7800 = *38·54%*.

III, 10. Determination of the strength of glacial acetic acid.—Weigh a dry, stoppered 50 ml. flask, introduce about 2 g. of glacial acetic acid and weigh again. Add about 20 ml. of water and transfer the solution quantitatively to a 250 ml. graduated flask. Wash the small flask several times with water and add the washings to the volumetric flask. Make up to the mark with distilled, preferably boiled-out, water. Shake the flask well to ensure thorough mixing. Titrate 25 ml. portions of the acid with 0·1*N* standard sodium hydroxide, using phenolphthalein or thymol blue as indicator.

$$\mathrm{NaOH + H.C_2H_3O_2 = Na.C_2H_3O_2 + H_2O.}$$
$$1 \text{ Ml. } N \text{ NaOH} \equiv 0{\cdot}06005 \text{ g. } \mathrm{H.C_2H_3O_2}.$$

Calculate the percentage of $\mathrm{H.C_2H_3O_2}$ in the sample of glacial acetic acid.

Note on the determination of the acetic acid content of vinegar. Vinegar usually contains 4 to 5 per cent of acetic acid. Weigh out about 20 g. of vinegar as described above, and make up to 100 ml. in a graduated flask. Remove 25 ml. with a pipette, dilute with an equal volume of water, add a few drops of phenolphthalein, and titrate with standard 0·1*N* sodium hydroxide solution. As a result of the dilution of the vinegar, its natural colour will be so reduced that it will not interfere with the colour change of the indicator. Calculate the acetic acid content of the vinegar, and express your result in g. of acetic acid per 100 ml.

III, 11. Determination of sulphuric acid in the concentrated acid.—Accurately weigh a small glass-stoppered weighing bottle, and add from a clean, *dry* 2 ml. pipette or measuring cylinder 0·7 to 0·8 ml. of the concentrated acid. Restopper the bottle immediately and reweigh accurately.* Place about 100 ml. of water in a 250 ml. volumetric flask, and insert a short-necked funnel in the mouth of the flask. Pour the weighed acid into the funnel, and, without removing the weighing bottle, wash it thoroughly both inside and outside with a stream of water from the wash bottle. Rinse the funnel thoroughly and remove it. Dilute nearly to the mark, and after 1 to 2 hours, when the solution has acquired the laboratory temperature, make up exactly to the mark. Shake and mix thoroughly. Titrate 25 ml. portions against standard 0·1*N* sodium hydroxide, using methyl orange or methyl orange-indigo carmine as indicator.

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* Alternatively, a weight pipette (Fig. 2-23, *a*) may be used. See, however, Section III, 12.

From the results calculate the percentage by weight of H_2SO_4 in the original concentrated acid.

$$1 \text{ Ml. } N \text{ NaOH} \equiv 0{\cdot}04904 \text{ g. } H_2SO_4.$$

III, 12. Determination of sulphuric acid in the fuming acid (oleum).—Fuming sulphuric acid may be considered as a mixture of sulphur trioxide and sulphuric acid, although it may contain pyrosulphuric acid $H_2S_2O_7$; if rich in sulphur trioxide, it is solid. The acid must not be exposed to the atmosphere during weighing and until it is diluted with water, as it is extremely hygroscopic. The **Lunge-Rey pipette** (Fig. 2-23, *b*) is particularly suitable for this determination ; the lower part of the pipette is protected by a ground-on test tube.

Weigh the complete dry pipette (it may be suspended from the balance by means of a thin silver wire). Close tap **2**, open tap **1**, and produce a slight vacuum in the bulb by applying suction (water pump, etc.), and then close stop-cock **1**. Dip the dry point of the pipette into the fuming acid (solid oleum must first be melted by warming gently), and cautiously open the lower stop-cock. As soon as the acid has entered the widened part of the pipette below the lower bulb, close tap **2**. Replace the test tube **4**, and weigh again. The increase in weight will give the weight of acid taken ; this should be about 1 g. Place about 100 ml. of distilled water in a beaker and cautiously dip the point of the pipette in the water ; open first tap **1** and then tap **2**, and allow the acid to run into the beaker. Wash the pipette thoroughly with distilled water. Transfer the contents of the beaker to a 250 ml. volumetric flask, make up to the mark, and shake well. Complete the determination as in Section **III, 11.**

Calculate the percentage of SO_3 in the sample of oleum.

III, 13. Determination of carbon dioxide in the atmosphere. —*Discussion.* The method to be described is due to Pettenkofer, as modified by Hesse. The carbon dioxide in a known volume of air is absorbed by excess of standard baryta solution, and the excess of the latter is determined by titration against standard oxalic acid or, better, hydrochloric acid, using phenolphthalein as indicator.

Procedure. The sample of air is collected in a thick-walled conical flask of 500 ml. or 1000 ml. capacity. The flask is fitted with a 2-holed rubber stopper, the holes being closed by glass-rod plugs ; a mark is made on the flask at the point where the rubber stopper ends. The capacity of the flask up to the point at which the rubber stopper reaches into the neck is determined by filling with water at a known temperature to this mark.

Fill the flask with air by aspiration with a rubber aspirator, or by filling it with distilled water and then pouring the water out slowly, or by any other convenient method: note the temperature and pressure of the air in the vessel. Add a five-fold excess of standard barium hydroxide solution (Section **III, 8**) by removing both glass plugs from the stopper and inserting the tip of the baryta solution burette into one of the holes; remove the burette and replace both glass plugs. Shake the vessel gently for about 20 minutes, and allow to stand for one hour. Remove both plugs, add a few drops of phenolphthalein, insert the tip of a burette containing standard hydrochloric acid (0·02 to 0·1*N*) into one of the holes, and titrate the excess of barium hydroxide present. Repeat the determination with another sample of air.

Compute the volume of standard alkali which has reacted with the carbon dioxide. From this volume and the known volume of the air less the volume of baryta solution added, calculate the percentage of CO_2 in the air.

$$1 \text{ Ml. } 0{\cdot}1N \text{ Ba(OH)}_2 \equiv 1{\cdot}119 \text{ ml. of } CO_2 \text{ at N.T.P.}$$

III, 14. Determination of a mixture of carbonate and hydroxide. Analysis of commercial caustic soda.—*Discussion.* Two methods may be used for this analysis. In the first method the total alkali (carbonate + hydroxide) is determined by titration with standard acid, using methyl orange, methyl orange-indigo carmine, or bromo-phenol blue as indicator. The carbonate is precipitated with a slight excess of barium chloride solution, and, without filtering,* the solution is titrated against standard acid with thymol blue or phenolphthalein as indicator. The latter titration gives the hydroxide content, and by subtracting this from the first titration, the volume of acid required for the carbonate is obtained.

$$Na_2CO_3 + BaCl_2 = BaCO_3 \text{ (insoluble)} + 2NaCl;$$
$$BaCl_2 + 2NaOH = Ba(OH)_2 \text{ (soluble)} + 2NaCl.$$

---

* The strong alkalinity of the soluble sodium carbonate due to hydrolysis is replaced by that (*p*H 8·6) due to a saturated solution of the sparingly soluble barium carbonate; hence phenolphthalein or thymol blue can then be employed as indicators.

The second method utilises two indicators. It has been stated in Section **I, 37** that the *p*H of half neutralised sodium carbonate, *i.e.*, at the sodium bicarbonate stage, is about 8·3, but the *p*H changes comparatively slowly in the neighbourhood of the equivalence point (compare Fig. 1-11), consequently the indicator colour change with phenolphthalein (*p*H range 8·3–10·0) or thymol blue (*p*H range (base) 8·0–9·6) is not too sharp. This difficulty may be surmounted by using a comparison solution containing sodium bicarbonate of approximately the same concentration as the unknown and the same volume of indicator. A simpler method is to employ a mixed indicator (Section **I, 29**) composed of 6 parts of thymol blue and 1 part of cresol red ; this mixture is violet at *p*H 8·4, blue at *p*H 8·3, and rose at *p*H 8·2. With this mixed indicator the mixture has a violet colour in alkaline solution and changes to blue in the vicinity of the equivalence point ; in making the titration the acid is added slowly until the solution assumes a rose colour. At this stage all the hydroxide and half the carbonate (by conversion into bicarbonate) has been neutralised. Let the volume of standard acid consumed be *v* ml.

$$\mathrm{NaOH + HCl = NaCl + H_2O:}$$
$$\mathrm{Na_2CO_3 + HCl = NaHCO_3 + NaCl.}$$

Another titration is performed with methyl orange or methyl orange—indigo carmine as indicator. Let the volume of acid be *V* ml.

$$\mathrm{NaOH + HCl = NaCl + H_2O:}$$
$$\mathrm{Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.}$$

Then $V - 2(V{-}v)$ corresponds to the hydroxide, $2(V{-}v)$ to the carbonate, and V to the total alkali. To obtain satisfactory results by this method the solution titrated must be cold (as near 0°C as is practicable), and loss of carbon dioxide must be prevented as far as possible by keeping the tip of the burette immersed in the liquid.

Procedure A. Weigh out accurately in a glass-stoppered weighing bottle about 2·5 g. of commercial sodium hydroxide (*e.g.*, in flake form). Transfer quantitatively to a 500 ml. volumetric flask and make up to the mark. Shake the flask well. Titrate 25 ml. or 50 ml. of this solution with standard 0·1*N* hydrochloric acid, using methyl yellow, methyl orange, or methyl orange-indigo carmine as indicator. Carry out two or three titrations : these should not differ by more than

0·1 ml. This gives the total alkalinity (hydroxide + carbonate). Warm another 25 ml. or 50 ml. of the solution to 70°C, and add 10 per cent barium chloride solution slowly from a burette or pipette in *slight* excess, *i.e.*, until no further precipitate is produced. Cool to room temperature, add a few drops of phenolphthalein to the solution and titrate very slowly and with constant stirring with standard 0·1*N* hydrochloric acid ; the end point is reached when the colour just changes from pink to colourless. If thymol blue is used as indicator, the colour change is from blue to yellow. The amount of acid used corresponds to the hydroxide present.

This method yields only approximate results because of the precipitation of basic barium carbonate in the presence of hydroxide. More accurate results are obtained by considering the above titration as a preliminary one in order to ascertain the approximate hydroxide content, and then carrying out another titration as follows. Treat 25 or 50 ml. of the solution with sufficient standard hydrochloric acid to neutralise most of the hydroxide, then heat and precipitate as before. Under these conditions, practically pure barium carbonate is precipitated.

$$1 \text{ Ml. } N \text{ HCl} \equiv 0{\cdot}0401 \text{ g. NaOH.}$$

$$1 \text{ Ml. } N \text{ HCl} \equiv 0{\cdot}05300 \text{ g. } Na_2CO_3.$$

Procedure B. The experimental details for the preparation of the initial solution are similar to those given under *Procedure A*. Titrate 25 ml. or 50 ml. of the cold solution with standard 0·1*N* hydrochloric acid and methyl orange, methyl orange-indigo carmine, or bromo-phenol blue as indicator. Titrate another 25 ml. or 50 ml. of the cold solution, diluted with an equal volume of water, slowly against the standard acid with phenolphthalein or, better, with the thymol blue-cresol red mixed indicator ; in the latter case, the colour at the end point is rose.

Calculate the result as described in the *Discussion* above.

III, 15. Determination of a mixture of carbonate and bicarbonate.—The two methods available for this estimation and modifications of those described in the previous Section for hydroxide-carbonate mixtures. In the first procedure, which is particularly valuable when the sample contains relatively large amounts of carbonate and small amounts of bicarbonate, the total alkali is first determined in one portion of the solution by titration against standard 0·1*N* hydrochloric acid with methyl orange, methyl orange-indigo carmine, or bromo-phenol blue as indicator :

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2;$$
$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

Let this volume correspond to V ml. N HCl. To another sample, a measured excess of standard 0·1*N* sodium hydroxide (free from carbonate) over that required to transform the bicarbonate to carbonate is added.

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

A slight excess of 10 per cent barium chloride solution is added to the hot solution to precipitate the carbonate as barium carbonate, and the excess of sodium hydroxide solution immediately determined without filtering off the precipitate by titration with the same standard acid ; phenolphthalein or thymol blue is used as indicator. If the volume of excess of sodium hydroxide solution added be equivalent to v ml. of N sodium hydroxide and v' ml. N acid corresponds to the excess of the latter, then $v-v'$ = bicarbonate, and $V - (v-v')$ = carbonate.

In the second procedure a portion of the cold solution is slowly titrated with standard 0·1*N* hydrochloric acid, using phenolphthalein or, better, the thymol blue-cresol red mixed indicator. This (say, M ml.) corresponds to half the carbonate (compare Section **III, 14**) :

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

Another sample is then titrated against the same standard acid with methyl orange, methyl orange-indigo carmine or bromophenol blue as indicator. The volume of acid used (say, m ml.) corresponds to carbonate + bicarbonate. Hence $2M$ = carbonate, and $m-2M$ = bicarbonate.

For practice the student should employ sodium sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$ (approx.), or else should use an artificial mixture prepared from 4 g. of A.R. potassium carbonate and 1 g. of A.R. sodium bicarbonate. The experimental details are similar to those given in Section **III, 14**.

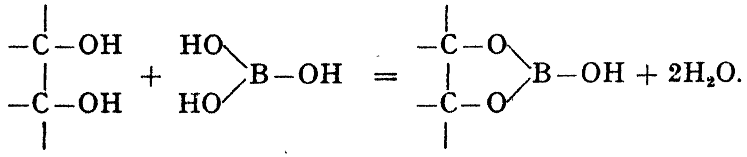
III, 16. Determination of phosphoric acid in commercial ortho-phosphoric acid.—*Discussion.* Phosphoric acid is a tribasic acid ; the *p*H at the equivalence point in 0·1*N* solutions corresponding to the primary, secondary and tertiary stages of ionisation are approximately 4·6, 9·7 and 12·6 respectively (compare Section **I, 37**). The *p*H changes in the neighbourhood of the equivalence points are not, however, very marked (see Fig. 1-10). For the first stage (*p*H 4·6) we may employ methyl orange or methyl orange-indigo carmine mixture (*p*H range 3·1–4·4) or bromo-cresol green (*p*H range 3·8–5·4), but it is best to use a solution of potassium or sodium dihydrogen phosphate containing the same amount of indicator for comparison. For the second stage (*p*H 9·7) phenolphthalein (*p*H range 8·3–10·0) is only approximate, thymolphthalein (*p*H range 9·3–10·5) is better, but the best indicator is a mixture of phenolphthalein (2 parts) and α-naphtholphthalein (1 part), which gives a change point from pale rose through green to violet at *p*H 9·6. For the third stage (*p*H 12·6) no satisfactory indicator is known. If titration be carried out to the second stage, and then calcium chloride solution be added to precipitate the trivalent ion as formed, titration as a tribasic acid is possible with thymolphthalein or the mixed indicator.

Procedure. Weigh out accurately in a ground-stoppered weighing bottle about 2 g. of commercial syrupy phosphoric acid. Transfer quantitatively to a 250 ml. volumetric flask and make up to the mark. Shake well. Titrate 25 ml. portions with standard carbonate-free sodium hydroxide, using thymolphthalein or, preferably, α-naphtholphthalein-phenolphthalein as indicator. Carry out two or three titrations ; these should not differ by more than 0·1 ml.

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O.$$
$$1 \text{ Ml. } N \text{ NaOH} = 0{\cdot}04902 \text{ g. } H_3PO_4.$$

Calculate the percentage of H_3PO_4 in the sample.

III, 17. Determination of boric acid and borax.—*Discussion.* Boric acid acts as a weak monobasic acid ($K_a = 5{\cdot}8 \times 10^{-10}$) ; it cannot therefore be titrated accurately with $0{\cdot}1N$ standard alkali (compare Section **I, 34**). However, by the addition of certain organic polyhydroxy compounds, such as glycerol, mannitol, dextrose or invert sugar, it is transformed into a relatively strong monobasic acid, probably of the type :



$$\begin{array}{l} | \\ -C-OH \\ | \\ -C-OH \\ | \end{array} + \begin{array}{l} HO \\ HO \end{array}\!\!>B-OH = \begin{array}{l} | \\ -C-O \\ | \\ -C-O \\ | \end{array}\!\!>B-OH + 2H_2O.$$

Glycerol is widely employed; the commercial substance is often acidic, consequently it is necessary to make the diluted glycerol neutral to phenolphthalein by adding sodium hydroxide solution. Mannitol (mannite) is more effective and has the advantage of being a solid and does not materially increase the volume of the solution being titrated: 0·5 to 0·7 g. of mannitol to 10 ml. of solution is a convenient quantity.

$$\text{H [boric acid complex]} + \text{NaOH} = \text{Na [boric acid complex]} + H_2O.$$

$$1 \text{ ml. } N \text{ NaOH} \equiv 0{\cdot}06184 \text{ g. } H_3BO_3.$$

The method may be applied to boric acid of commerce and to borates. The technical boric acid may contain ammonium salts. It is best to dissolve 1 g. in hot water, add a slight excess of sodium carbonate, boil the solution down to half bulk in order to expel ammonia, filter any precipitate which may be formed, and to titrate the filtrate against standard 0·1N sodium hydroxide with phenolphthalein as indicator.

For practice in the titration the student may employ commercial borax. This may be titrated against standard acid with methyl orange or with methyl orange-indigo carmine mixed indicator (Section **I, 37**):

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

$$1 \text{ Ml. } N \text{ HCl} \equiv 0{\cdot}10065 \text{ g. } Na_2B_4O_7.$$

The liberated boric acid may then be titrated against standard alkali in the presence of mannitol with phenolphthalein as indicator. Carbonic acid must be absent as it leads to high results.

$$1 \text{ Ml. } N \text{ NaOH} \equiv 0{\cdot}06184 \text{ g. } H_3BO_3 \equiv 0{\cdot}05033 \text{ g. } Na_2B_4O_7.$$

Procedure. Weigh out accurately about 4 g. of commercial borax, transfer it quantitatively to a 250 ml. volumetric flask, and make up to the mark. Shake well. Titrate 25 ml. of this solution with standard 0·1N hydrochloric acid, using methyl orange or methyl orange-indigo carmine as indicator.

To another 25 ml. of the solution, add the quantity of standard hydrochloric acid determined in the previous titration,* cover the beaker or conical flask with a clock glass or Fisher " speedyvap " beaker cover, heat to simmering temperature for 10 minutes to expel carbon dioxide (prolonged vigorous boiling may cause loss of boric acid which is volatile in steam), cool the solution to room temperature, and add just sufficient standard sodium hydroxide solution to restore the transition colour of the original indicator. Then introduce about 2 g. of mannitol, and shake until dissolved ; add a few drops of phenolphthalein and titrate against standard 0·1*N* carbonate-free sodium hydroxide to the first permanent faint pink colour. Add a further 0·5 g. of mannitol ; if the solution becomes colourless, add more standard sodium hydroxide until the pink colour reappears. Repeat the process until the addition of mannitol has no effect upon the end point.

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* If carbonate is absent, mannitol may be added at this stage, and the titration completed with standard sodium hydroxide solution in the presence of phenolphthalein.

Calculate the percentage of $Na_2B_4O_7$ in the sample from the results of both titrations.

III, 18. Determination of ammonia in an ammonium salt.—*Discussion.* Two methods, the direct and indirect, may be used for this determination. In the **direct method,** a solution of the ammonium salt is treated with a solution of a strong base (*e.g.*, sodium hydroxide) and the mixture distilled. Ammonia is quantitatively expelled and is absorbed in an excess of standard acid. The excess of acid is back-titrated in the presence of methyl red (or methyl orange, methyl orange-indigo carmine, bromo-phenol blue or bromo-cresol green). Each ml. of *N* acid consumed in the reaction is equivalent to 0·017032 g. NH_3.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

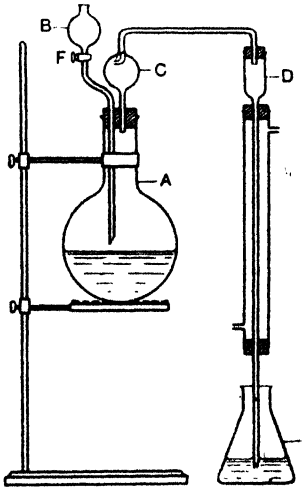

Fig. 3-3.

In the **indirect method,** the ammonium salt (other than the carbonate or bicarbonate) is boiled with a known excess of standard sodium hydroxide solution. The boiling is continued until no more ammonia escapes with the steam. The excess of sodium hydroxide is titrated against standard acid, using methyl red (or methyl orange-indigo carmine) as indicator.

Procedure (**direct method**). Fit up the apparatus shown in Fig. 3-3. **A** is a 1 litre Pyrex or Jena glass flask provided with a two-holed rubber stopper which carries a tap funnel **B** and a glass spray trap **C**. The purpose of the trap is to prevent any droplets of sodium hydroxide solution being driven over in the subsequent distillation. **D** is a Liebig's condenser attached to the trap by means of a rubber bung, and **E** is a 350 ml. Pyrex conical flask which serves as a receiver. For practice, weigh out 1·5 g. of A.R. ammonium chloride or of crude sal ammoniac, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake thoroughly. Transfer 50 ml. of the solution into the distillation flask and dilute with 200 ml. of water ; add a few pieces (*ca.* 1 g.) of pure zinc foil or granulated zinc to promote regular ebullition in the subsequent distillation. Place 100 ml. of standard 0·1*N* hydrochloric acid in the receiver and adjust the flask so that the end of the condenser just dips into the acid. Make sure that all the corks are fitting tightly. Place 100 ml. of 10 per cent sodium hydroxide solution in the funnel. Run the sodium hydroxide solution into the flask by opening the tap **F** ; close the tap as soon as all the alkali has entered. Heat the flask so that the contents boil gently. Continue the distillation for 30 to 40 minutes by which time all the ammonia should have passed over into the receiver. Open the tap **F** before removing the flame. Disconnect the trap from the top of the condenser. Lower the receiver and rinse the condenser with a little water. Add a few drops of methyl red and titrate the excess of acid in the solution with standard 0·1*N* sodium hydroxide. Repeat the determination.

Calculate the percentage of NH_3 in the solid ammonium salt employed.

Procedure (**indirect method**). Weigh out accurately 0·1 to 0·2 g. of the ammonium salt into a 350 ml. Pyrex or Jena glass conical flask, and add 100 ml. of standard 0·1*N* sodium hydroxide. Place a small funnel in the neck of the flask in order to prevent mechanical loss, and boil the mixture until a piece of filter paper moistened with mercurous nitrate solution is no longer turned black. Cool the solution, add a few drops of methyl red, and titrate with standard 0·1*N* hydrochloric acid. Repeat the determination.

Calculate the percentage of NH_3 in the substance.

III, 19. Determination of nitrates (sodium nitrate in Chile saltpetre).—*Discussion.* Nitrates are reduced to ammonia by means of aluminium, zinc or, most conveniently, by Devarda's alloy (50Cu, 5Al, 5Zn) in strongly alkaline solution :

$$3NO_3^- + 8Al + 5OH^- + 2H_2O = 8AlO_2^- + 3NH_3.$$

The ammonia is distilled into excess of standard acid as in Section **III, 18.**

Nitrites are similarly reduced and must be allowed for if nitrate alone is to be determined.

Procedure. Weigh out accurately about 1 g. of Chile saltpetre. Dissolve it in water and transfer the solution quantitatively to the distillation flask of Fig. 3-3. Dilute to about 240 ml. Add 3 g. of pure finely-divided Devarda's alloy (it should all pass a 20-mesh sieve). Fit up the apparatus completely (all connexions must be made with rubber bungs), and place 75–100 ml. of standard 0·2*N* hydrochloric acid in the receiver (500 ml. Pyrex conical flask). Introduce 10 ml. of 20 per cent sodium hydroxide solution through the funnel and immediately close the tap. Warm *gently* to start the reaction, and allow the apparatus to stand for an hour, by which time the evolution of hydrogen should have practically ceased and the reduction of nitrate to ammonia be complete. Then boil the liquid gently and continue the distillation until 40–50 ml. of liquid remain in the distillation flask. Open the tap before removing the flame. Wash the condenser with a little distilled water, and titrate the contents of the receiver and the washings against standard 0·2*N* sodium hydroxide, using methyl red as indicator. Repeat the determination. For very accurate work, it is recommended that a blank test be carried out with distilled water.

Calculate the percentage of $NaNO_3$ in Chile saltpetre.

$$1 \text{ Ml. } N \text{ HCl} \equiv 0{\cdot}08501 \text{ g. } NaNO_3.$$

Note. Nitrates can be reduced in neutral solution quantitatively to ammonia with Arndt's alloy (60 per cent Mg; 40 per cent Cu); any slight spurting of the boiling liquid does not vitiate the titration. Here the distillation flasks will contain 50 ml. of the above nitrate solution, 150 ml. of water, 2 g. of hydrated magnesium chloride, and 5 g. of the finely-divided alloy. The whole is boiled until about two thirds of the liquid has passed over. The distillate is collected in 50 ml. of 0·1*N* hydrochloric acid.

III, 20. Determination of nitrogen by Kjeldahl's method.—*Discussion.* This process is so widely employed in industrial and research laboratories that an account of it must be included in this book. The principle of the method is the conversion of the nitrogen of the nitrogenous substance by boiling with concentrated sulphuric acid into ammonia, which is fixed by the excess of acid as ammonium sulphate. The latter is determined by adding an excess of caustic alkali to the solution after digestion with the acid, and distilling off the liberated ammonia into standard acid as detailed in Section **III, 18.** Simple digestion with concentrated sulphuric acid is, however, a slow process and various modifications have been suggested to increase the speed of the reaction. These include the addition of potassium sulphate, which raises the boiling point of the acid (Kjeldahl-Gunning process), and of catalysts, such as mercury, mercuric oxide, anhydrous copper sulphate, selenium, or a mixture of equal parts of ferrous sulphate and selenium. The simple process works well for nitrogen determinations in proteins and also in amines and amides, but is not applicable to nitro, azo, hydrazo, and cyano compounds without modification. In the presence of nitrates, there is a danger of loss of nitric acid: salicylic acid is then added to the sulphuric acid (proportion: 1 g. to 30 ml.), which fixes the nitric acid as nitro-salicylic acid. Upon the addition of zinc dust (1 g.) or of anhydrous sodium thiosulphate (5 g.), the nitro-salicylic acid is reduced to the amino compound, which can then be estimated by the Kjeldahl process.

Procedure. The determination may be carried out with 1·5 to 2·0 g. of flour or with acetanilide. Weigh out accurately about 0·1 g. of acetanilide into a dry Pyrex Kjeldahl flask—a round-bottomed flask with a long narrow neck. Add 10 g. of A.R. potassium sulphate, 0·2 g. of selenium or 0·5 g. of anhydrous copper sulphate or 0·5 g. of equal parts of ferrous sulphate and selenium, and pour 25 ml. of concentrated sulphuric acid into the flask in such a way as to wash down any solid adhering to the neck. Shake until the contents are well mixed. Support the flask on a hole (4·5 cm. in diameter) in a piece of asbestos board, and incline the neck at an angle of about 60°. Close the flask with a loosely-fitting glass stopper elongated to a point and having a balloon-shaped top: a small funnel or a flat reagent bottle stopper will serve the same purpose. Heat the flask *in a fume cupboard* with a small flame. When frothing has ceased, increase the flame until the mixture boils gently. Continue the heating for 30 minutes *after* the solution has become colourless or clear (usually 90 to 120 minutes), and then allow the solution to cool. When *cold*, add about 200 ml. of water carefully and with frequent shaking. Transfer completely to the ammonia distillation apparatus (Fig. 3-3), add a little pure zinc, followed by excess of sodium hydroxide solution. Distil off the ammonia into excess of standard acid exactly as described in Section **III, 18.** Carry out a blank determination exactly as above, but with the nitrogen-containing sample omitted subtract the " blank," if any.

Calculate the percentage of nitrogen in the solid.

Note. If mercury (0·7 g.) or mercuric oxide (1 g.) is employed as catalyst, it is necessary to add 25 ml. of a solution containing 8 g. of sodium thiosulphate or 4 g. of potassium sulphide per 100 ml. before distilling in order to decompose the mercuri-ammonium compounds formed.

PRECIPITATION AND COMPLEX-FORMATION REACTIONS

III, 21. General discussion.—The reader should be familiar with the theory of precipitation and complex formation processes given in Sections **I, 40** to **I, 42.** With this theoretical groundwork, he should experience little difficulty in carrying out the following determinations in an intelligent manner, and also to modify them when occasion demands.

The standard solutions employed include those of silver nitrate, sodium chloride, potassium or ammonium thiocyanate, and potassium cyanide.

III, 22. Preparation of 0·1*N* silver nitrate.—*Discussion.* Very pure silver can be obtained commercially, and a standard solution can be prepared by dissolving a known weight (say, 10·788 g.) in pure dilute nitric acid in a conical flask having a funnel in the neck to prevent mechanical loss, and making up to a known volume (say, 1 litre for a 0·1*N* solution). The presence of acid must, however, be avoided in such determinations as that of Mohr (Section **I, 42A**) with potassium chromate as indicator or in estimations employing adsorption indicators (Section **I, 42C**). It is therefore preferable to employ a neutral solution by dissolving silver nitrate (equivalent weight, 169·89) in water.

A.R. Silver nitrate has a purity of at least 99·9 per cent, so that a standard solution can be prepared by direct weighing. If, however, the ordinary recrystallised silver nitrate be employed, or if an additional check of the normality of the silver nitrate solution is required, standardisation may be effected with pure sodium chloride:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

The ordinary A.R. sodium chloride has a purity of 99·9 to 100·0 per cent*; the substance is therefore an excellent primary standard. Sodium chloride is very slightly hygroscopic, and for accurate work it is best to dry the finely-powdered solid in an electric oven at 250° to 350°C for 1 to 2 hours, and allow it to cool in a desiccator.†

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* Sodium chloride is supplied by the Mallinckrodt Chemical Works, U.S.A., of 99·97 per cent purity, and by the Bureau of Analysed Samples, as a British Chemical Standard, of 99·96 per cent purity. See Appendix, Section **A, 9.**

† For the most precise work, the powdered solid should be dried in an electric muffle furnace at 500° to 600°C and then allowed to cool in a desiccator. This high temperature is unnecessary for work of ordinary accuracy (within 0·1 per cent).

Procedure A. **From A.R. silver nitrate.** Dry some finely-powdered A.R. silver nitrate at 150°C for 2 hours and allow it to cool in a desiccator. Weigh out accurately 8·496 g.*, dissolve it in water and make up to 500 ml. in a volumetric flask. This gives an 0·1000*N* solution. Alternatively, about 8·5 g. of the pure, dry silver nitrate may be weighed out accurately, dissolved in 500 ml. of water in a graduated flask, and the exact normality computed from the weight of silver nitrate employed.

Procedure B. **From recrystallised silver nitrate.** Weigh out about 8·5 g. of the silver nitrate, dissolve it in water, and make up to 500 ml. in a volumetric flask. Shake well.

Solutions of silver nitrate should be protected from light; they are best stored in amber-coloured glass bottles.

III, 23. Standardisation of the silver nitrate solution.—Sodium chloride has an equivalent weight of 58·46. A 0·1000*N* solution is prepared by weighing out 2·923 g. of the pure dry salt (*e.g.*, A.R., but see Discussion in Section **III, 22**) and dissolving it in 500 ml. of water in a volumetric flask. Alternatively about 2·9 g. of the pure salt is accurately weighed out, dissolved in 500 ml. of water in a graduated flask, and the exact normality calculated from the weight of sodium chloride employed.

A. With potassium chromate as indicator. The Mohr titration. The student is referred to Section **I, 42B** for the detailed theory of the titration. Prepare the *indicator solution* by dissolving 5 g. of A.R. potassium chromate in 100 ml. of water. The final volume of the solution in the titration is 50 to 100 ml., and 1 ml. of the indicator solution is used, so that the indicator concentration in the actual titration is 0·005 to 0·0025 molar.

Pipette 25 ml. of the standard 0·1*N* sodium chloride into a 250 ml. conical flask resting upon a white tile (1), and add 1 ml. of the indicator solution (preferably with a 1 ml. pipette). Add the silver nitrate solution slowly from a burette, swirling the liquid constantly, until the red colour formed by the addition of each drop begins to disappear more slowly: this is an indication that most of the chloride has been precipitated. Continue the addition dropwise until a faint but distinct change in colour occurs. This *faint* reddish-brown colour should persist after brisk shaking. If the end point is overstepped (production of a deep reddish-brown colour), add more of the chloride solution and titrate again. Determine the indicator blank correction by adding 1 ml. of the indicator to a volume of water equal to the final volume in the titration (2), and then silver nitrate solution until the colour of the blank matches that of the solution titrated. The indicator blank correction, which should not amount to more than 0·03 to 0·10 ml. silver nitrate, is deducted from the volume of silver nitrate used in the titration. Repeat the titration with two further 25 ml. portions of the sodium chloride solution (3). The various titrations should agree within 0·1 ml.

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* This weight should be multiplied by the purity factor of the A.R. silver nitrate, *e.g.*, by 1/0·999.

Calculate the normality of the silver nitrate solution (see Section **III, 4A**).

Notes. 1. The end point is very readily detected in a large porcelain basin or in a casserole. The solution is stirred with a short glass stirring rod.

2. A better blank is obtained by adding about 0·5 g. of A.R calcium carbonate before determining the correction. This give an inert-white precipitate similar to that obtained in the titration of chlorides and materially assists in matching the colour tints.

3. See Note 1 to *Procedure A* in Section **III, 6.**

B. With an adsorption indicator. *Discussion.*—The detailed theory of the process is given in Section **I, 42C.** Both fluorescein and dichlorofluorescein are suitable for the titration of chlorides. In both cases the end point is reached when the white precipitate in the greenish-yellow solution suddenly assumes a pronounced reddish tint. The change is reversible upon the addition of chloride. With fluorescein the solution must be neutral or only faintly acidic with acetic acid ; acid solutions should be treated with a slight excess of sodium acetate. The chloride solution should be diluted to about 0·01 to 0·05*N*, for if it is more concentrated the precipitate coagulates too soon and interferes. Fluorescein cannot be used in solutions more dilute than 0·005*N*. With more dilute solutions resort must be made to dichlorofluorescein, which possesses other advantages over fluorescein. Dichlorofluorescein gives good results in very dilute solutions (*e.g.*, for drinking water) and is applicable in the presence of acetic acid and in weakly acid solutions. For this reason the chlorides of copper, nickel, manganese, zinc, aluminium and magnesium, which cannot be titrated according to the method of Mohr, can be determined by a direct titration when dichlorofluorescein is used as indicator.

For the reverse titration (chloride into silver nitrate), tartrazine (4 drops of a 0·5 per cent solution per 100 ml.) is a good indicator. At the end point, the almost colourless liquid assumes a green colour.

The indicator solutions are prepared as follows:

Fluorescein. Dissolve 0·1 g. of fluorescein in 100 ml. of 70 per cent alcohol, or dissolve 0·1 g. of sodium fluoresceinate in 100 ml. of water.

Dichlorofluorescein. Dissolve 0·1 g. of dichlorofluorescein in 100 ml. of 60 to 70 per cent alcohol, or dissolve 0·1 g. of sodium dichlorofluoresceinate in 100 ml. of water.

Procedure. Pipette 25 ml. of the standard 0·1*N* sodium chloride into a 250 ml. conical flask. Add 10 drops of either fluorescein or dichlorofluorescein indicator, and titrate against the silver nitrate solution with constant rotation in a diffuse light. As the end point is approached, the silver chloride coagulates appreciably and the local development of a pink colour upon the addition of a drop of the silver nitrate solution becomes more and more pronounced. Continue the addition of the silver nitrate solution until the precipitate suddenly assumes a pronounced pink or red colour. Repeat the titration with two other 25 ml. portions of the chloride solution. Individual titrations should agree within 0·1 ml.

Calculate the normality of the silver nitrate solution.

III, 24. Determination of chlorides.—Either the Mohr titration or the adsorption indicator method may be used for the estimation of chlorides in neutral solution by titration with standard 0·1*N* silver nitrate. If the solution is acid, neutralisation may be effected with chloride-free calcium carbonate, sodium bicarbonate or borax; the A.R. substances are suitable. Mineral acid may also be removed by neutralising most of the acid with ammonia solution and then adding an excess of A.R. ammonium acetate. Titration of the neutral solution prepared with calcium carbonate by the adsorption indicator method is rendered more facile by the addition of 5 ml. of 2 per cent dextrin solution; this offsets the coagulating effect of the calcium ion. If the solution is basic, it may be neutralised with chloride-free nitric acid, using phenolphthalein as indicator.

III, 25. Determination of bromides.—*Discussion.* The Mohr titration may be applied to the estimation of bromides. The most suitable adsorption indicator is eosin, although fluorescein may be used but is subject to the limitations detailed under Chlorides in Section **III, 23B.** Eosin is serviceable in dilute solutions and even in the presence of 0·1*N* nitric acid, but in general, however, acetic acid solutions are to be preferred.

The **eosin indicator** is prepared by dissolving 0·1 g. of eosin in 100 ml. of 70 per cent alcohol, or by dissolving 0·1 g. of the sodium salt in 100 ml. of water.

For the reverse titration (bromide into silver nitrate), rhodamine 6G (10 drops of a 0·1 per cent solution of the chloride) is an excellent indicator. The solution is best rendered 0·5*N* with respect to nitric acid, and should be 0·01 to 0·02*N* with respect to silver. The precipitate acquires a violet colour at the end point.

Another method for the volumetric determination of bromides, which utilises an adsorption indicator (bromo-phenol blue), involves titration with **mercurous nitrate solution.** The solid reagent is deliquescent and cannot therefore be obtained in a state of appropriate purity for accurate weighing : the A.R. product $HgNO_3,H_2O$ has a purity of not less than 95 per cent. 30 Grams of A.R. mercurous nitrate are dissolved in water containing a little nitric acid, and made up to 1 litre in a volumetric flask. The reagent is first standardised against 0·1*N* potassium bromide, prepared by dissolving 11·902 g. of A.R. potassium bromide in 1 litre of water. 25 Ml. of the bromide solution is diluted with an equal volume of water and treated with a few drops of a 0·1 per cent solution of bromo-phenol blue. Titration is then carried out with the mercurous nitrate solution until the yellowish tint on the precipitate suddenly changes to lilac. A similar titration is then carried out with the unknown bromide solution.

For practice in the use of eosin, the student may determine the purity of potassium bromide, preferably of A.R. quality.

Procedure. Weigh out accurately about 3 g. of the potassium bromide, dissolve it in water, and make up to 250 ml. in a graduated flask. Pipette 25 ml. of the well-mixed solution into a 250 ml. conical flask, add 75 ml. of water, a few ml. of 6*N*-acetic acid and 10 drops of eosin solution. Titrate against the standard 0·1*N* silver nitrate, with constant agitation, in a diffuse light. The silver bromide flocculates approximately 1 per cent before the equivalence point, and the local development of red colour becomes more and more pronounced upon the addition of silver nitrate solution. Continue the addition dropwise with vigorous swirling of the liquid until the precipitate suddenly assumes a pronounced magenta colour. Repeat the titration with two other 25 ml. portions of the bromide solution.

Calculate the purity of the sample.

$$1 \text{ Ml. } N \text{ AgNO}_3 \equiv 0{\cdot}07992 \text{ g. Br} \equiv 0{\cdot}1190 \text{ g. KBr.}$$

III, 26. Determination of chlorides and bromides with standard mercurous perchlorate solution.*—*Discussion.* Mercurous perchlorate, with bromo-phenol blue as adsorption indicator, may be used for the determination of chlorides and bromides. It can be applied in acid solution ; its solutions are reasonably stable when kept in the dark (the chloride titre is reduced by only 0·1 per cent after 4 months), they are easy to prepare, are free from interfering mercuric ions (compare mercurous nitrate solution, Section **III, 25**), and give sharp end points which coincide almost exactly with the equivalence points. The colour change at the end point is from creamy white to lilac ; the best results are obtained if the addition of the indicator is delayed until near the end point.

Nitric, perchloric and acetic acids have no effect if the total acid concentration does not exceed 0·04N ; higher concentrations of acid inhibit the colour change. Sulphuric acid and sulphates cause a high titre ; this error is completely eliminated by adding an excess of lead nitrate to the *boiling* solution ; the lead sulphate need not be filtered off before titration. The only cations which interfere are those of silver and mercuric mercury ; the latter reduces the titre by an amount proportional to their concentration, due presumably to the removal of some of the halide ions as undissociated mercuric halide.

Procedure. **A. Preparation of approximately 0·1*N* mercurous perchlorate.** Shake the following materials vigorously together at intervals over a period of 1 hour : 22 g. of A.R. red mercuric oxide, 45 g. of perchloric acid (*d* 1·5 ; 60 per cent), 50 ml. of water, and 30 g. of pure mercury. From time to time withdraw a few drops of the liquid, dilute, treat with sodium chloride solution, and filter : the preparation is complete when the filtrate from the test portion gives no precipitate with hydrogen sulphide. Decant or filter the liquid from the excess of mercury, and dilute to 2 litres. Keep the solution in the dark ; if it is exposed to light, decomposition into mercury and mercuric perchlorate occurs.

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* W. Pugh, 1937.

B. Standardisation. Deci-normal sodium chloride (Section **III, 23**) or potassium bromide (Section **III, 25**) may be employed. 25 Ml. of either solution is diluted to 100 ml. in a conical flask, 0·5 ml. of bromo-phenol blue (0·05 per cent solution in water) added, and the mercurous perchlorate solution run in from a burette until the colour of the precipitate changes from creamy white to lilac. It is best to add the indicator near the end point.

C. Use in determination of chlorides and bromides. Dilute the solution of the halide to 100 ml. If sulphates are present, boil, add 10 to 20 ml. of 5 per cent lead nitrate solution, and cool. Add 1 drop of bromo-phenol blue, then ammonia or sodium carbonate solution until the indicator turns faintly blue, and titrate with the $0{\cdot}1N$ (or $0{\cdot}05N$) mercurous perchlorate. Just before the end point is attained, add 0·5 ml. of bromo-phenol blue, and continue the titration until the colour of the precipitate changes to lilac.

For practice, the student may determine the percentage of chlorine in A.R. crystallised barium chloride.

III, 27. Determination of iodides.—*Discussion.* The Mohr method cannot be applied to the titration of iodides (and also of thiocyanates), because of adsorption phenomena and the difficulty of distinguishing the colour change of the potassium chromate. Eosin is a suitable adsorption indicator, but di-iododimethylfluorescein is better. Eosin is employed as described under bromides (Section **III, 25**).

The **di-iododimethylfluorescein indicator** is prepared by dissolving 1·0 g. in 100 ml. of 70 per cent alcohol. The colour change is from an orange-red to a blue-red on the precipitate.

For practice, the student may determine the purity of potassium iodide, preferably of A.R. quality.

Procedure. Weigh out accurately about 4 g. of the potassium iodide, dissolve it in water and make up to 250 ml. in a volumetric flask. Pipette 25 ml. of the well-mixed solution into a 250 ml. conical flask, add 75 ml. of water and 1 ml. of di-iododimethylfluorescein indicator. Titrate against the standard $0{\cdot}1N$ silver nitrate as detailed under Chlorides (Section **III, 23B**). Flocculation of the silver iodide occurs about 1 per cent before the end point, and the colour change at the end point is from orange-red to blue-red. Repeat with two other 25 ml. portions of the solution.

Calculate the purity of the sample.

$$1 \text{ Ml. } N\ AgNO_3 \equiv 0{\cdot}1269 \text{ g. I} \equiv 0{\cdot}1660 \text{ g. KI.}$$

III, 28. Determination of thiocyanates.—These may be estimated with adsorption indicators exactly as for Chlorides and Bromides. Further experimental details are therefore superfluous. For another method, see Section **III, 43.**

III, 29. Determination of mixtures of halides with adsorption indicators.—A. Chloride and iodide in admixtures. These two ions differ considerably in the ease with which they are adsorbed on the corresponding silver halide. This makes it possible to select adsorption indicators which will permit of the estimation of chloride and iodide in the presence of one another. Thus the iodide may be determined with di-iododimethylfluorescein (Section **III, 27**) by titration with standard 0·1N silver nitrate, and the iodide + chloride by a similar titration with fluorescein. Chloride is obtained by difference. If a large excess of chloride is present the result for iodide may be as much as 1 per cent high. If, however, Rose Bengal (dichlorotetraiodofluorescein) is used as indicator (colour change, carmine red to blue-red) in the presence of ammonium carbonate, the iodide titration is exact.

B. Bromide and iodide in admixture. The total halide (bromide + iodide) is determined by titration with standard 0·1N silver nitrate with eosin or fluorescein as indicator. The iodide is estimated by titration with 0·01 to 0·2N silver nitrate, using di-iodidimethylfluorescein as indicator. Bromide is obtained by difference.

Numerous adsorption indicators have been suggested for various purposes, but a full treatment is outside the scope of this work.*

III, 30. Determination of mixtures of halides by an indirect method.—*Discussion.* The method is applicable to the determination of a mixture of two salts having the same anion (*e.g.*, sodium and potassium chlorides) or the same cation (*e.g.*, potassium chloride and potassium bromide). Let us first suppose that it is desired to estimate the amount of sodium and potassium chlorides in a mixture of the two salts. A known weight (w_1 g.) of the solid mixture is taken, and the total chloride is determined with standard 0·1N silver nitrate, using Mohr's method or an adsorption indicator. Let w_2 g. of silver nitrate be required for the complete precipitation of

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* An excellent account is given by K. Fajans in the Chapter entitled "Adsorption indicators for precipitation reactions" in W. Bottger–R. E. Oesper *Newer Methods of Volumetric Chemical Analysis*, 1938, pp. 203–250 (Van Nostrand; Chapman and Hall).

w_1 g. of the mixture, which contains x g. of NaCl and y g. of KCl. Then:

$$x + y = w_1;$$

$$\frac{169{\cdot}89\,x}{58{\cdot}46} + \frac{169{\cdot}89\,y}{74{\cdot}56} = w_2.$$

Upon solving these two simultaneous equations, the values for x and y are deduced.

Let us now suppose that the estimation of potassium chloride and potassium bromide in admixture is desired. The total halide is determined by Mohr's method or with an adsorption indicator. Let the weight of the mixture be w_3 g., w_4 g. be the weight of silver nitrate required for complete precipitation, p g. be the weight of the potassium chloride, and q g. be the weight of the potassium bromide. Then:

$$p + q = w_3;$$

$$\frac{169{\cdot}98\,p}{74{\cdot}56} + \frac{169{\cdot}89\,q}{119{\cdot}02} = w_4.$$

The values of p and q can be obtained by solving the simultaneous equations.

It can be shown* that the method depends upon the difference between the equivalent weights of the two components of the mixture and that *inter alia* it is most satisfactory when the two constituents are present in approximately equal proportions.

For practice, the student may prepare for himself, or obtain from the teacher, a mixture of equal weights of potassium and sodium chlorides or of potassium chloride and bromide, and determine the proportions of each by titration with standard 0·1N silver nitrate. The experimental details for the titrations have been given in previous Sections.

III, 31. Preparation and use of 0·1*N* ammonium or potassium thiocyanate. Titrations according to Volhard's method. —*Discussion.* Volhard's original method (1874, 1878) for the determination of silver in *dilute nitric acid* solution by titration with standard thiocyanate solution in the presence of a ferric salt as indicator has proved of great value not only for silver estimations, but also in numerous indirect analyses. The theory of the Volhard process has been given in Section **I, 42B.** In this connexion it must be pointed out that the concentration of the nitric acid should be from 1 to 10 per cent by volume (strong nitric acid retards the formation of the " ferric thiocyanate ") and at a temperature not exceeding 25°C (higher temperatures tend to bleach the colour of the indicator). The solutions must be free from nitrous acid, which gives a red colour with thiocyanic acid, and may be mistaken for " ferric thiocyanate." Pure nitric acid is prepared by diluting the usual pure (*e.g.*, A.R.) acid with about one-fourth of its volume of water and boiling until perfectly colourless ; this eliminates any lower oxides of nitrogen which may be present.

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* See H. A. Fales *Inorganic Quantitative Analysis*, 1925, p. 204 (Century).

The method may be applied to those anions (*e.g.*, chloride, bromide and iodide) which are completely precipitated by silver and are sparingly soluble in dilute nitric acid. Excess of standard silver nitrate solution is added to the solution containing free nitric acid, and the residual silver nitrate solution is titrated with standard thiocyanate solution. This is sometimes termed the **residual process.** Anions whose silver salts are slightly soluble in water, but which are soluble in nitric acid, such as phosphate, arsenate, chromate, sulphide and oxalate, may be precipitated in neutral solution with an excess of standard silver nitrate solution. The precipitate is filtered off, thoroughly washed, dissolved in dilute nitric acid and the silver titrated with thiocyanate solution. Alternatively, the residual silver nitrate in the filtrate from the precipitation may be determined with thiocyanate solution after acidification with dilute nitric acid.

Both ammonium and potassium thiocyanates are usually available as deliquescent solids ; the A.R. products are, however, free from chlorides and other interfering substances. An approximately 0·1*N* is therefore first prepared and this is standardised by titration against standard 0·1*N* silver nitrate.

Procedure. Weigh out about 9 g. of A.R. ammonium thiocyanate, or 11 g. of A.R. potassium thiocyanate, and dissolve it in 1 litre of water in a volumetric flask. Shake well.

Standardisation. Use 0·1*N* silver nitrate, which has been prepared and standardised as described in Section **III, 23.**

The **indicator solution** consists of a cold saturated solution of A.R. ferric ammonium sulphate in water (about 40 per cent) to which a little 6*N* nitric acid has been added. 1 Ml. of this solution is employed for each titration.

Pipette 25 ml. of the standard 0·1*N* silver nitrate into a 250 ml. conical flask, add 5 ml. of 6*N* nitric acid and 1 ml.

of the indicator solution. Run in the potassium or ammonium thiocyanate solution from a burette. At first a white precipitate is produced, rendering the liquid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud, which quickly disappears on shaking. As the end point approaches, the precipitate becomes flocculent and settles easily ; finally one drop of the thiocyanate solution produces a faint brown colour, which no longer disappears upon shaking. This is the end point. The indicator blank amounts to 0·01 ml. of 0·1N silver nitrate. It is essential to shake vigorously during the titration in order to obtain correct results. Repeat the titration with two other 25 ml. portions of the silver nitrate solution. Individual titrations should agree within 0·1 ml.

Calculate the normality of the thiocyanate solution from the known normality of the silver nitrate solution (for details of calculation, see Sections **I, 24** and **III, 4A**). It will be found that the thiocyanate solution is a little stronger than 0·1N. The volume of water that must be added to make the solution exactly 0·1000N is computed as described in *Example 15* (Section **I, 24**).

The standard solution thus prepared remains of the same strength for a very long period if evaporation is prevented.

III, 32. Determination of silver in a silver alloy.—A silver three-penny piece (or any other small silver coin) is suitable for this determination. Clean the coin with emery cloth and weigh it accurately. Place it in a 250 ml. conical flask, add 5 ml. of water and 10 ml. of concentrated nitric acid ; place a funnel in the mouth of the flask to avoid mechanical loss. Warm the flask gently until the coin has dissolved. Add a little water and boil for 5 minutes in order to expel oxides of nitrogen. Transfer the cold solution quantitatively to a 100 ml. standard flask and make up to the mark with distilled water. Titrate 25 ml. portions of the solution with standard 0·1N thiocyanate as described in Section **III, 31.**

Calculate the percentage of silver in the alloy.

$$1 \text{ Ml. } N \text{ KCNS or } NH_4CNS \equiv 0{\cdot}10788 \text{ g. Ag.}$$

NOTE. The presence of metals whose salts are colourless does not influence the accuracy of the determination, except that mercury and palladium must be absent since their thiocyanates are insoluble. Salts of metals (*e.g.*, nickel and cobalt) which are coloured must not be present to any considerable extent. Copper does not interfere provided it does not form more than about 40 per cent of the alloy.

III, 33. Determination of chlorides (Volhard's method).—*Discussion.* The chloride solution is treated with an excess of standard silver nitrate solution, and the residual silver nitrate determined by titration with standard thiocyanate solution. Now silver chloride is more soluble than silver thiocyanate and would react with the thiocyanate thus :

$$AgCl + CNS^- \rightleftharpoons AgCNS + Cl^-$$

(the theory of this process is given in Section **I, 42B**). It is therefore necessary to remove the silver chloride by filtration. The filtration may be avoided by the addition of a little nitrobenzene (about 1 ml. for each 0·05 g. of chloride) ; the silver chloride is probably surrounded by a film of nitrobenzene.

For practice in this estimation, the student may determine the HCl content of concentrated hydrochloric acid.

Procedure A (**HCl content of concentrated hydrochloric acid**). Ordinary concentrated hydrochloric acid is usually 10 to 11*N*, and must be diluted first. Measure out accurately 10 ml. of the concentrated acid from a burette into a 1 litre volumetric flask and make up to the mark with distilled water. Shake well. Pipette 25 ml. into a 250 ml. conical flask, add 5 ml. of 6*N* nitric acid and then add 30 ml. of standard 0·1*N* silver nitrate (or sufficient to give 2 to 5 ml. excess). Shake to coagulate the precipitate, filter through a quantitative filter paper (or through a Gooch or sintered glass crucible), and wash thoroughly with very dilute nitric acid. Add 1 ml. of the saturated ferric alum solution to the combined filtrate and washings, and titrate the residual silver nitrate with standard 0·1*N* thiocyanate. Repeat the titration with two other 25 ml. portions of the chloride solution.

Calculate the volume of standard 0·1*N* silver nitrate that has rested with the hydrochloric acid, and therefrom the percentage of HCl in the sample employed.

Procedure B. Pipette 25 ml. of the diluted solution into a 250 ml. conical flask containing 5 ml. of 6*N* nitric acid. Add a slight excess (2 to 5 ml.) of standard 0·1*N* silver nitrate (about 30 ml.) from a burette. Then add 2 to 3 ml. of pure (*e.g.*, A.R.) nitrobenzene and 1 ml. of the ferric alum indicator, and shake vigorously to coagulate the precipitate. Titrate the residual silver nitrate with standard 0·1*N* thiocyanate until a permanent faint reddish-brown colouration appears. Repeat the titration with two other 25 ml. portions of the solution.

From the volume of silver nitrate solution added, subtract the volume of silver nitrate solution that is equivalent to the volume of standard thiocyanate required. Then calculate the percentage of HCl in the sample.

1 Ml. *N* $AgNO_3$ = 0·03546 g. Cl. = 0·03647 g. HCl.

III, 34. Determination of bromides (Volhard's method).—Silver bromide is less soluble than silver thiocyanate so that it is not necessary to filter off the silver bromide (compare previous Section). The bromide solution is acidified with dilute nitric acid, an excess of standard 0·1*N* silver nitrate added, the mixture thoroughly shaken, and the residual silver nitrate determined with standard 0·1*N* thiocyanate, using ferric alum as indicator.

1 Ml. *N* $AgNO_3$ = 0·07992 g. Br = 0·08093 g. HBr.

For practice, the student may determine the percentage of HBr in the constant b.p. hydrobromic acid, or of bromine in potassium bromide, preferably of A.R. quality (compare Section **III, 23**).

III, 35. Determination of iodides (Volhard's method).—Here also there is no need to filter off the silver halide since silver iodide is very much less soluble than silver thiocyanate. In this estimation the iodide solution must be very dilute in order to reduce adsorption effects. The dilute iodide solution (*ca.* 300 ml.), acidified with dilute nitric acid, is treated very slowly and with vigorous stirring or shaking with standard 0·1*N* silver nitrate until the yellow precipitate coagulates and the supernatant liquid appears colourless. Silver nitrate is then present in excess. 1 Ml. of saturated iron alum solution is added, and the residual silver nitrate is titrated against standard 0·1*N* thiocyanate.

1 Ml. *N* $AgNO_3$ = 0.1269 g. I = 0·1279 g. HI.

For practice, the student may determine the percentage of HI in the constant boiling point hydriodic acid or of iodide in potassium iodide, preferably of A.R. quality (compare Section **III, 27**).

III, 36. Determination of hyposulphites.*—*Discussion.* The method depends upon the reduction of ammoniacal silver nitrate solution by the hyposulphite to metallic silver; the silver is dissolved in nitric acid and titrated against standard thiocyanate solution, using ferric alum as indicator.

$$Na_2S_2O_4 + 2AgNO_3 + 2H_2O = 2Ag + 2NaHSO_3 + 2HNO_3.$$

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* Also called hydrosulphites.

The procedure has the advantage that the solid is weighed directly into the reagent, and thus avoids the rapid atmospheric oxidation of the solution.

Procedure (**hyposulphite content of commercial "hydros"**). Weigh out accurately about 0·4 g. of powdered "hydros" (sodium hyposulphite, usually $Na_2S_2O_4,H_2O$) from a stoppered weighing bottle into a dry beaker, and cover it with at least a two-fold excess of ammoniacal silver nitrate solution (prepared by the addition of dilute ammonia solution in excess of that required to re-dissolve the silver hydroxide first formed). As the salt dissolves, it is at once oxidised and metallic silver is precipitated. It is essential not to warm the solution. When dissolution of the salt is complete, filter the precipitated silver on asbestos in a Gooch crucible (or through a sintered glass or porous porcelain crucible), and wash it with dilute ammonia solution containing a little ammonium nitrate to prevent peptisation of the finely-divided metal. Transfer the crucible and contents to the beaker in which precipitation took place, dissolve the metal in nitric acid, and boil the solution to remove nitrous fumes. Filter the resultant solution through a sintered glass crucible, dilute the filtrate, add 1 ml. of saturated ferric alum solution, and titrate with standard 0·1*N* thiocyanate.

Calculate the percentage of $Na_2S_2O_4$ in the sample.

1 Ml. *N* NH_4CNS (or KCNS) $\equiv$ 0·08706 g. $Na_2S_2O_4$.

III, 37. Determination of cobalt.—*Discussion.* This method is based upon the formation of the compound $[Co(C_5H_5N)_4](CNS)_2$ (Sections **I, 62L** and **IV, 33D**). Excess of a standard solution of ammonium thiocyanate is added to a solution of the cobaltous salt containing a little pyridine, the precipitated complex salt is filtered off, and the excess of thiocyanate titrated with standard silver nitrate solution.

Procedure. The sample should contain 0·05 to 0·1 g. of cobalt as cobaltous salt. Dissolve it in 150 ml. of water in a 250 ml. volumetric flask, acidify with dilute nitric acid (to litmus), add 3 ml. of pure pyridine, and excess of standard 0·1*N* ammonium thiocyanate (1). The cobalt is precipitated as $[Co(C_5H_5N)_4](CNS)_2$, which settles readily and filters easily. Dilute to the mark, and mix thoroughly. Filter a portion of the solution through a quantitative filter paper, and discard the first few ml. of the filtrate. Transfer 50 ml. of the filtrate to a beaker or conical flask, dilute to 100 ml., add 1 ml.

of concentrated nitric acid, and then a known excess of standard $0{\cdot}1N$ silver nitrate. Add 5 ml. of ferric indicator (2), and titrate the excess of silver nitrate with $0{\cdot}1N$ ammonium thiocyanate in the usual way (Section **III, 31**).

Calculate the weight of cobalt w from the formula :

$$w = [\text{ml. of } NH_4CNS \times N - 5(\text{ml. of } AgNO_3 \times N)]\ 0{\cdot}02947.$$

Notes. 1. Standardise the $0{\cdot}1N$ ammonium thiocyanate against standard $0{\cdot}1N$ silver nitrate : the latter may be standardised, if necessary, against A.R. sodium chloride.

2. Dissolve 5 g. of A.R. iron alum in a mixture of 40 ml. of water and 10 ml. of $6N$ nitric acid.

III, 38. Determination of nickel.—The procedure is similar to that given in the preceding Section for Cobalt. The complex has the formula $[Ni(C_5H_5N)_4](CNS)_2$ (compare Section **IV, 32C**). The weight of nickel w is calculated from the formula :

$$w = [\text{ml. of } NH_4CNS \times N - 5(\text{ml. of } AgNO_3 \times N)]\ 0{\cdot}02935.$$

Note. The method may also be applied to the determination of copper (Section **IV, 19E**), cadmium (Section **IV, 18D**), and zinc (Section **IV, 34D**).

III, 39. Determination of fluoride as lead chlorofluoride.—*Discussion.* This method is based upon the precipitation of lead chlorofluoride PbClF, which can be weighed as such, or, more conveniently, the chlorine is determined by Volhard's method from which the fluorine content can be calculated. The advantages of the method are : the precipitate is granular, settles readily and is easily filtered ; the factor for conversion to fluorine is low ; the volumetric procedure is carried out at pH 3·6 to 5·6, so that substances which might be coprecipitated, such as phosphates, sulphates, chromates and carbonates, do not interfere. Aluminium must be entirely absent since even very small quantities cause low results ; a similar effect is produced by boron (> 0·05 g.), ammonium (> 0·5 g.), and sodium or potassium (>10 g.). Iron must be removed, but zinc is without effect. Silica does not vitiate method, but causes difficulties in filtration.

For practice, the student may determine the percentage of fluorine in sodium fluoride.

Procedure. Weigh out accurately about 1·5 g. of dry sodium fluoride, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 25 ml. of the solution into a 400 ml. beaker*, add 2 drops of bromo-phenol blue indicator, 3 ml. of 10 per cent sodium chloride and dilute the mixture to 250 ml. Add dilute nitric acid until the colour just changes to yellow, and then add dilute sodium hydroxide solution until the colour just changes to blue. Treat with 1 ml. of concentrated hydrochloric acid, then with 5·0 g. of A.R. lead nitrate, and heat on the steam bath. Stir gently until the lead nitrate has dissolved, and then immediately add 5·0 g. of crystallised sodium acetate and stir vigorously. Digest on the steam bath for 30 minutes, with occasional stirring, and allow to stand overnight.

Meanwhile, a washing solution of lead chlorofluoride is prepared as follows. Add a solution of 10 g. of lead nitrate in 200 ml. of water to 100 ml. of a solution containing 1·0 g. of sodium fluoride and 2 ml. of concentrated hydrochloric acid, mix it thoroughly, and allow the precipitate to settle. Decant the supernatant liquid, wash the precipitate by decantation with 5 portions of water, each of about 200 ml. Finally add 1 litre of water to the precipitate, shake the mixture at intervals during an hour, allow the precipitate to settle, and filter the liquid. Further quantities of wash liquid may be prepared as needed by treating the precipitate with fresh portions of water. The solubility of lead chlorofluoride in water is 0·325 g. at 25°C.

Separate the original precipitate by decantation through a Whatman No. 542 or No. 42 paper. Transfer the precipitate to the filter, wash once with cold water, four or five times with the saturated solution of lead chlorofluoride and finally once more with cold water. Transfer the precipitate and paper to the beaker in which precipitation was made, stir the paper to a pulp in 100 ml. of 5 per cent nitric acid, and heat on the steam bath until the precipitate has dissolved (5 minutes). Add a slight excess of standard 0·1*N* silver nitrate, digest on the steam bath for a further 30 minutes, and allow to cool to room temperature while protected from the light. Filter the precipitate of silver chloride through a sintered glass crucible, wash with a little cold water, and titrate the residual silver nitrate in the filtrate and washings with standard 0·1*N* thiocyanate. Subtract the amount of silver found in the filtrate from that originally added. The difference represents the amount of silver that was required to combine with the chlorine in the lead chlorofluoride precipitate.

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* The details apply to a volume of solution corresponding to 0·01 to 0·1 g. of fluorine.

Calculate the percentage of fluorine in the sample.

1 Ml. N $AgNO_3$ ≡ 0·01900 g. F.

III, 40. Determination of arsenic as silver arsenate.—*Discussion.* Arsenates in solution are precipitated as silver arsenate Ag_3AsO_4 by the addition of neutral silver nitrate solution : the solution must be neutral or if slightly acid, an excess of sodium acetate must be present to reduce the acidity; if strongly acid, most of the acid should be neutralised by aqueous sodium hydroxide. The silver arsenate is dissolved in dilute nitric acid, and the silver titrated with standard thiocyanate solution. The silver arsenate has nearly 6 times the weight of the arsenic, hence quite small amounts of arsenic may be determined by this procedure.

Arsenites must first be oxidised by treatment with nitric acid. Small amounts of antimony and tin do not interfere, but chromates, phosphates, molybdates, tungstates and vanadates, which precipitate as the silver salts, should be absent. An excessive amount of ammonium salts has a solvent action on the silver arsenate.

A general method applicable to all arsenic compounds will be described.

Procedure. Fuse 0·5 g. (or less, according to the amount of As present) of the finely-powdered substance with 3 to 5 g. of a 1:1 mixture of A.R. sodium carbonate and A.R. potassium nitrate, placing about one-third of the mixture on top of the charge, or, alternatively, use 10 to 12 times the weight of sodium peroxide. Extract the cooled melt with hot water, and filter. Acidify the filtrate, containing the soluble arsenate, with dilute nitric acid, boil to expel carbon dioxide, and cool. Add sufficient sodium hydroxide solution to give an alkaline reaction to phenolphthalein, and then discharge the red colour from the solution by just acidifying with acetic acid. Add a slight excess of silver nitrate solution with vigorous stirring, and allow the precipitate to settle in the dark. Pour off the supernatant liquid through a sintered glass crucible, wash the precipitate by decantation with cold distilled water, transfer the precipitate to the crucible, and wash it free from silver nitrate solution. Wash out the receiver thoroughly. Dissolve the silver arsenate in dilute nitric acid (*ca.* N) (which leaves any silver chloride undissolved), wash with very dilute nitric acid, and make up the filtrate and washings to 250 ml. in a volumetric flask. Titrate a convenient aliquot portion with standard ammonium (or potassium) thiocyanate solution in the presence of ferric alum as indicator (Section **III, 31**). Calculate the percentage of arsenic in the sample.

1 Ml. N thiocyanate $\equiv$ 0·02947 g. of As.

III, 41. Determination of cyanides.—*Discussion.* The theory of the titration of cyanides with silver nitrate solution according to Liebig (1851) has been given in Section **I, 41.** All silver salts except the sulphide are readily soluble in excess of a solution of an alkali cyanide, hence chloride, bromide and iodide do not interfere. The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide is often precipitated in a curdy form which does not readily redissolve, and, moreover, the end point is not easy to detect with accuracy.

There are two methods for overcoming these disadvantages. In the first the precipitation of silver argentocyanide at the end point can be avoided by the addition of ammonia solution, in which it is readily soluble :

$$Ag[Ag(CN)_2] + 4NH_4OH = 2[Ag(NH_3)_2]CN^* + 4H_2O.$$

If a little potassium iodide solution is added before the titration is commenced, the sparingly soluble silver iodide, which is insoluble in ammonia solution, will be precipitated at the end point.

$$2[Ag(NH_3)_2]CN + 2KI + 4H_2O = 2AgI + 2KCN + 4NH_4OH.$$

At the end point, the cyanide, in which silver iodide is soluble, is no longer present to keep it in solution, and since, unlike the silver argentocyanide, it is insoluble in ammonia solution, silver iodide is precipitated. The precipitation is best seen by viewing against a black background.

In the second method diphenylcarbazide is employed as an adsorption indicator. The end point is marked by the pink colour becoming pale violet (almost colourless) on the colloidal precipitate in dilute solution (*ca.* 0·01N) before the opalescence is visible. In 0·1N solutions, the colour change is observed on the precipitated particles of silver argentocyanide.

For practice, the student may determine the percentage of KCN in potassium cyanide (single salt).

NOTE. Potassium cyanide and all other cyanides are deadly poisons and extreme care must be taken in their use.

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* Or $[Ag(NH_3)_2]^+ + [Ag(CN)_2]^-$.

Procedure A. **(KCN in potassium cyanide).** Weigh out accurately about 3·5 g. of potassium cyanide (single salt) from a glass-stoppered weighing bottle, dissolve it in water and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of this solution **by means of a burette and NOT a pipette** to a 250 ml. conical flask, add 75 ml. of water, 5 to 6 ml. of $6N$ ammonia solution, and 2 ml. of 10 per cent potassium iodide solution. Place the flask on a sheet of black paper, and titrate with standard $0{\cdot}1N$ silver nitrate. Add the silver nitrate solution dropwise as soon as the yellow silver iodide shows any signs of persisting. When 1 drop produces a permanent turbidity, the end point has been reached. Repeat the titration with two other 25 ml. portions of the cyanide solution.

Calculate the KCN content of the sample.

1 Ml. N $AgNO_3 \equiv 0{\cdot}05204$ g. CN $\equiv 0{\cdot}1304$ g. KCN.

Procedure B. Transfer 25 ml. of the cyanide solution, prepared as detailed in *Procedure A*, **by means of a burette and NOT a pipette** into a 250 ml. conical flask, add two to three drops of the diphenylcarbazide indicator, and titrate against the standard $0{\cdot}1N$ silver nitrate until a permanent violet colour is just produced. Repeat the titration with two other 25 ml. portions of the cyanide solution.

The **diphenylcarbazide indicator** is prepared by dissolving 0·1 g. of diphenylcarbazide in 100 ml. of alcohol.

Calculate the percentage of KCN in the sample.

III, 42. Determination of nickel by potassium cyanide.—*Discussion.* This method depends upon the fact that nickel ions can react with potassium cyanide in slightly ammoniacal solution to form a complex anion, $[Ni(CN)_4]^{--}$:

$$[Ni(NH_3)_6]Cl_2 + 4KCN + 6H_2O = K_2[Ni(CN)_4] + 6NH_4OH + 2KCl.$$

If the ammoniacal solution of nickel contains a little silver iodide in suspension and potassium cyanide solution is added, the turbidity will not disappear until all the nickel has been converted into the complex cyanide. The slightest excess of cyanide is therefore indicated by the clearing of the liquid; this excess may be determined exactly by adding standard silver nitrate solution until the turbidity is reproduced.

$$AgI + 2KCN = K[Ag(CN)_2] + KI;$$
$$Ag^+ + I^- = AgI.$$

Copper, cobalt and zinc, which form complex cyanides, must be absent ; the addition of alkali pyrophosphate, however, renders zinc harmless. Aluminium, manganese and iron are kept in solution by the addition of citric acid, tartaric acid or sodium pyrophosphate.

The potassium cyanide solution is standardised against standard $0{\cdot}1N$ silver nitrate as described in Section **III, 41.** It is evident that :

$$AgNO_3 \equiv 2KCN \equiv Ni/2,$$

$$\text{i.e., } 1 \text{ ml. } N\ AgNO_3 \equiv 0{\cdot}1304 \text{ g. } KCN \equiv 0{\cdot}02935 \text{ g. Ni.}$$

For practice in this determination, the student may determine the percentage of nickel (*a*) in pure nickel ammonium sulphate and (*b*) in a steel.

Procedure (**Ni in nickel ammonium sulphate**) Dissolve 14 g. of A.R. potassium cyanide in 1 litre of distilled water in a volumetric flask, and shake well. Prepare a solution of 10 g. of A.R. potassium iodide in 100 ml. of water. Standardise the potassium cyanide solution against standard $0{\cdot}1N$ silver nitrate (Section **III, 41**).

Weigh out accurately about 5 g. of pure nickel ammonium sulphate $NiSO_4,(NH_4)_2SO_4,6H_2O$*, dissolve it in water containing a little dilute sulphuric acid, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 25 ml. of this solution into a 250 ml. conical flask, add 125 ml. of water, followed by $6N$ ammonia solution until the fluid smells slightly of it, and then add a further 3 ml. If a precipitate forms, it will redissolve if a little ammonium chloride solution is added. Then add 5 ml. of the potassium iodide solution and a *small* measured volume, say 0·5 to 1 ml., of the standard $0{\cdot}1N$ silver nitrate. The silver iodide produced should cause the liquid to become cloudy. Titrate with the standard potassium cyanide solution from a burette until the turbidity just disappears. This will take place when the potassium cyanide added is equivalent to the nickel in the solution plus the silver in the known volume (0·5 to 1 ml.) of silver nitrate solution added. Add standard $0{\cdot}1N$ silver nitrate dropwise from a burette until the cloudiness due to silver iodide reappears. The excess of potassium cyanide solution, which is equivalent to the silver nitrate solution, is thus accurately determined.

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* The A.R. product may be obtained, *e.g.*, from the Mallinckrodt Chemical Works, U.S.A. See Appendix, Section **A, 9.**

Repeat the titration with two other 25 ml. portions of the nickel solution.

Calculate the volume of the standard potassium cyanide solution which has reacted with the nickel, and therefrom the percentage of nickel in the sample.

Procedure **(Ni in nickel steel).** The most accurate method for the analysis of any steel containing nickel is to precipitate the nickel as the dimethylglyoxime complex, and to determine the nickel in the latter.

Weigh out accurately about 1 g. of the nickel steel* into a 350 ml. conical flask, add 15 ml. of $8N$ nitric acid, and place a funnel in the mouth of the flask to prevent mechanical loss. When the first violent action is over, boil gently until all the steel has dissolved, adding a little concentrated hydrochloric acid if necessary. Continue the boiling for 5 minutes in order to expel oxides of nitrogen. Dilute to 200 ml., and add 8 g. of pure tartaric acid. When all the tartaric acid has dissolved, neutralise with concentrated ammonia solution, and add *ca.* 1 ml. in excess. If any insoluble material is present, filter it through a quantitative filter paper, and wash the latter with hot water. Acidify the solution with hydrochloric acid, heat to 80°C and add 20 to 25 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Add ammonia solution until the liquid is slightly alkaline, and allow to stand for 30 to 60 minutes, preferably on a water bath. Filter the precipitate through a Gooch or Jena sintered glass crucible, and wash the precipitate thoroughly with hot water. Dissolve the precipitate in 25 ml. of $6N$ nitric acid, add 20 ml. of $9N$ sulphuric acid and boil for 20 minutes. Add 6 g. of citric acid, render the solution slightly ammoniacal, and, when cold, titrate the nickel as described above.

Calculate the percentage of nickel in the steel.

III, 43. Determination of thiocyanates.—*Discussion.* The method (H. E. Williams, 1939) consists in the titration of the thiocyanate in dilute nitric acid solution with a standard solution of mercuric nitrate, using a little iron alum solution as indicator. Immediately the thiocyanate is completely converted into the mercuric salt, the solution becomes water-white. The end point is very sharp.

The method may also be applied to the determination of

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* Either Ridsdale's " Nickel steel, No. 22 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Nickel Steel, T " (a British Chemical Standard) is suitable.

thiocyanate and chloride in admixture when the chloride is present in comparatively small amount (say, 5 per cent of the thiocyanate). The neutral solution containing the thiocyanate and chloride is treated with excess of bismuth nitrate solution. The precipitated bismuth oxychloride is separated, the filtrate acidified with dilute nitric acid, and the thiocyanate determined as above.

Procedure: The following solutions should be prepared:

***N*-Mercuric nitrate.** 100·3 Grams of dry A.R. mercury are heated in a 600 ml. beaker (*fume cupboard*) with 250 ml. of distilled water, and concentrated nitric acid is added until all the mercury is dissolved. The action of the acid is rather energetic, especially when hot, and the acid should be added a little at a time. The solution is boiled to drive off all nitrous fumes, cooled, transferred to a standardised litre flask, and diluted to 1000 ml. The 0·1*N* solution is prepared by diluting the *N* solution. Since the mercury is pure and can be accurately weighed, the solution requires no standardisation.

Mercuric sulphate may replace the nitrate, but offers no advantage; mercuric chloride cannot be used.

Dilute nitric acid. 150 Ml. of concentrated nitric acid are added to 400–500 ml. of distilled water, boiled to drive off nitrous gases, and diluted to 1000 ml.

Iron alum solution. 25 Grams of A.R. iron alum are dissolved in water, and diluted to 500 ml.

The solution containing about 0·2 g. of thiocyanate is diluted to 150–200 ml. with distilled water, and 10 ml. of the dilute nitric acid and 2 ml. of the iron alum solution are added. The solution is titrated against the 0·1*N* mercuric nitrate solution with constant agitation until the red colour of the ferric thiocyanate just disappears, leaving the solution water-white.

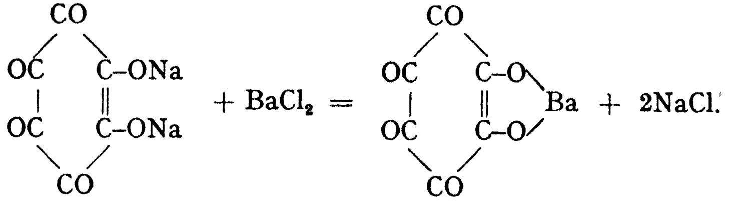
$$1 \text{ Ml. } 0{\cdot}1N \text{ Hg(NO}_3)_2 \equiv 0{\cdot}005808 \text{ g. CSN.}$$

Thiocyanate and chloride in admixture. A **solution of bismuth nitrate** is required and is prepared as follows. 10 Grams of pure crystallised bismuth nitrate and 50 ml. of A.R. glacial acetic acid are warmed in a 200 ml. beaker, and 30 ml. of distilled water are added gradually until complete dissolution has been effected, the solution being stirred between each addition. When the salt has completely dissolved, the solution is diluted to 500 ml. with distilled water. 10 Ml.

of this solution are required to precipitate approximately 0·01 g. of chloride, calculated as sodium chloride.

The neutral solution containing approximately 0·2 g. of thiocyanate and 0·01 g. of chloride (calculated as NaCl) is diluted to 150 ml. with distilled water, and 10 ml. of the bismuth nitrate solution are added. The mixture is shaken, left for 10–15 minutes in the cold, filtered through a quantitative filter paper, and the precipitate well washed. The filtrate should give no precipitate upon the addition of a few ml. of the bismuth nitrate solution. The filtrate is then acidified with dilute nitric acid, and, after adding 2 ml. of the iron solution, titrated with 0·1*N* mercuric nitrate solution as above. The chloride may be determined by any of the usual methods by dissolving the basic chloride on the filter paper in dilute nitric acid.

III, 44. Determination of barium and of sulphates. Barium solutions, weakly acid with hydrochloric acid, give a red precipitate of barium " rhodizonate " with a freshly-prepared solution of the sodium salt of rhodizonic acid (dihydroxydiquinoyl, $C_6O_4(OH)_2$) :



The solubility of the red compound is much greater than that of barium sulphate, hence upon the addition of a sulphate solution to a solution of a barium salt, the barium will be completely precipitated when the red colour changes to colourless (in weakly acid solution) or to yellow (in neutral solution). This forms the basis of a volumetric method for the determination of barium. To obtain the best results, it is advisable to work with concentrated solutions (volume up to 10 ml. — 0·2 to 0·5*N*).

The **indicator** is freshly prepared as required by dissolving 15 mg. of sodium " rhodizonate " in 5 ml. of water. Ten drops are used for each titration.

A. Barium. The concentrated solution of the barium salt (5 to 10 ml.) is treated with 10 drops of indicator and 1 to 2 ml. of alcohol. It is then titrated with vigorous shaking against (*a*) 0·2*N* potassium sulphate (prepared from the A.R.

solid) until the colour changes sharply from red to yellow, or (*b*) against $0{\cdot}2N$ sulphuric acid until the colour changes from red to colourless.

B. Sulphate. Sulphate in acid solution cannot be titrated directly against a solution of a barium salt, because rhodizonic acid is unstable and soon decomposes. A known excess of barium chloride solution ($0{\cdot}2$ to $0{\cdot}5N$) is added to the sulphate solution, and the excess of barium titrated as above. Here also the solutions should be concentrated ($0{\cdot}2$ to $0{\cdot}5N$) and the volume small (10 to 25 ml.).

Excellent results may be obtained as follows. A known volume of the neutral alkali sulphate solution (say, 10 to 20 ml.) is placed in a glass-stoppered conical flask, 1 g. of pure ammonium chloride added, followed by a known excess of $0{\cdot}2N$ barium chloride (prepared from the A.R. salt) and 10 drops of the freshly-prepared indicator. The mixture is thoroughly shaken, and 3 drops of 10 per cent hydrochloric acid added; the further addition of one-third the volume of alcohol improves the end point. The mixture is then titrated against $0{\cdot}2N$ potassium sulphate until the colour begins to fade. The alkali sulphate solution is then added dropwise, with vigorous shaking and waiting for a short time between the drops, until the red colour has completely disappeared. The titration is repeated until consistent results are obtained.

By subtracting the volume of $0{\cdot}2N$ potassium sulphate from that of the $0{\cdot}2N$ barium chloride originally employed, the volume of the latter equivalent to the sulphate present in the initial solution is found, since $\mathrm{Ba} \equiv \mathrm{SO_4}$.

OXIDATION-REDUCTION TITRATIONS. OXIDIMETRY AND REDUCTIMETRY

III, 45. General discussion.—The student should be familiar with the general theory of oxidation-reduction given in Chapter I ; in particular, he should read :

Section **I, 23**—Equivalent weights. Normal solutions.

Sections **I, 43** to **I, 53**—Theory of oxidation-reduction reactions (including potentiometric titration).

With this groundwork, he should experience no difficulty in carrying out oxidation-reduction titrations intelligently and, when once he has had practice in the fundamental simple titrations, the student should be in a position to apply his combined theoretical and practical knowledge to more complex cases and to various practical problems.

The standard solutions of oxidising agents employed in the titration of reducing agents include those of potassium permanganate, potassium dichromate, ceric sulphate, manganic sulphate, iodine, potassium iodate, potassium bromate, and chloramine-T. The standard solutions of reducing agents, used in the titration of oxidising agents, include those of sodium thiosulphate, arsenious oxide, sodium oxalate, oxalic acid, ferrous salts, titanous sulphate or chloride, chromous sulphate or chloride, and vanadous sulphate or chloride. The mode of use and applications of each of these will be given in the following Sections.

OXIDATIONS WITH POTASSIUM PERMANGANATE

III, 46. Discussion.—This valuable and powerful oxidising agent was first introduced into volumetric analysis by F. Margueritte in 1846 for the titration of ferrous iron. In *acid solutions*, the reduction can be represented by the following equation :

$$MnO_4^- + 8H^+ + 5\epsilon \rightleftharpoons Mn^{++} + 4H_2O,$$

from which it follows that the equivalent weight is one fifth of the formula weight (1/5 mol)*, or 158·03/5, or 31·606.

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* For elementary students, the equivalent weight may be deduced from the hypothetical equation :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

It follows that the equivalent weight is one fifth of the molecular weight ($KMnO_4/5$).

Sulphuric acid is the most suitable acid as it has no action upon permanganate in dilute solution. With hydrochloric acid, there is the likelihood of the reaction :

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O,$$

taking place, and some permanganate may be consumed in the formation of chlorine. This reaction is particularly liable to occur with iron salts unless special precautions are adopted (see below). With a small excess of free acid, a very dilute solution, low temperature and slow titration with constant shaking, the danger from this cause is minimised. There are, however, some titrations, such as those with arsenious oxide, trivalent antimony and hydrogen peroxide, which can be carried out with hydrochloric acid.

In the analysis of iron ores, solution is frequently effected in concentrated hydrochloric acid, the ferric iron is reduced with a slight excess of stannous chloride solution, and the excess of the latter removed with mercuric chloride solution (**Zimmerman-Reinhardt process**) : the ferrous iron is then determined in the resultant solution. To do this, it is best to add about 25 ml. of *Zimmermann and Reinhardt's solution*, which is prepared by dissolving 50 g. of crystallised manganese sulphate $MnSO_4,4H_2O$ in 250 ml. of water, adding a cooled mixture of 100 ml. of concentrated sulphuric acid and 300 ml. of water, followed by 100 ml. of syrupy phosphoric acid. The manganous sulphate lowers the oxidation potential of the permanganate (compare Sections **I, 46, 47** and Fig. I-17) and thereby makes it a weaker oxidising agent ; the tendency of the permanganate to oxidise chloride ions is thus reduced. The manganous ion also acts as a catalyst in promoting the speed of the reduction of the permanganate ion, and as a negative catalyst for the oxidation of the chloride ion. The phosphoric acid combines with the yellow ferric ions to form colourless complex ions, thus rendering the end point more clearly visible. The main purpose of the phosphoric acid is, however, to lower the oxidation potential of the ferric-ferrous system (Section **I, 46**) and thus to increase the reducing power of the ferrous iron.

For the titration of colourless or slightly coloured solutions, the use of an indicator is unnecessary, since as little as 0·01 ml. of 0·01*N* potassium permanganate imparts a pale pink colour to 100 ml. of water. The intensity of the colour in dilute solutions may be enhanced, if desired, by the addition of an oxidation-reduction indicator, such as diphenylamine, diphenylbenzidine, sodium diphenylamine sulphonate, tri-ortho-phenanthroline ferrous sulphate or *N*-phenylanthranilic acid, near the end point of the reaction ; this is usually not required.

Potassium permanganate also finds considerable application in *strongly* alkaline solutions. Here two consecutive partial reactions take place : (i) the relatively rapid reaction

$$MnO_4^- + \epsilon = MnO_4^{--},$$

and (ii) the relatively slow reaction

$$MnO_4^{--} + 2H_2O + 2\epsilon = MnO_2 + 4OH^-.$$

By suitably controlling the experimental conditions, it is possible to arrange that reaction (i) occurs almost exclusively ; the equivalent weight is then 1 mol. Excess of deci-molar potassium permanganate which is 1 to 2*N* with respect to sodium hydroxide is added to a solution of the substance to be oxidised. After 10 to 20 minutes the excess of permanganate is back-titrated either in an alkaline medium with a standard solution of sodium formate

$$(2MnO_4^- + 3OH^- + HCO_2^- = 2MnO_4^{--} + CO_3^{--} + 2H_2O)$$

or in an acid medium with oxalic acid.*

Potassium permanganate is not a primary standard. It is difficult to obtain the substance perfectly pure and free from manganese dioxide. Moreover, ordinary distilled water is likely to contain reducing substances (traces of organic matter, etc.) which will react with the potassium permanganate to form manganese dioxide. The presence of the latter is very objectionable because it catalyses the auto-decomposition of the permanganate solution on standing. For these reasons, potassium permanganate solution is never made up exactly by weight, but after removal of the manganese dioxide by filtration through purified asbestos or glass wool or through a sintered glass filter crucible (Jena, No. 4) is standardised by one of several methods. These methods include the use of the following substances : sodium oxalate $Na_2C_2O_4$, arsenious oxide As_2O_3, metallic iron, ferrous ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$, oxalic acid $H_2C_2O_4,2H_2O$, and potassium tetroxalate $KHC_2O_4,H_2C_2O_4,\ 2H_2O$.

Of these substances sodium oxalate was formerly regarded as the most trustworthy, since it is readily obtained pure and anhydrous. The U.S. Bureau of Standards supplies a product of 99·95 per cent guaranteed purity, and the ordinary A.R. substance has a purity of at least 99·9 per cent.* The experimental procedure hitherto employed was due to R. S. McBride (1912). A solution of the oxalate, acidified with dilute sulphuric acid and warmed to 80° to 90°C, was treated slowly (10 to 15 ml. per minute) and with constant stirring with the permanganate solution until the first permanent faint pink colour was obtained ; the temperature near the end point was not allowed to fall below 60°C. R. M. Fowler and H. A. Bright (1935) have, however, shown that with McBride's procedure the results may be 0·1 to 0·45 per cent high ; the titre depends upon the acidity, the temperature, the rate of addition of the permanganate solution, and upon the speed of stirring. These authors recommend *a more rapid* addition of 90 to 95 per cent of the permanganate solution (about 25 to 35 ml. per minute) to a solution of sodium oxalate in 2*N* sulphuric acid at 25° to 30°C, the solution is then warmed to 55° to 60°C and the titration completed, the last 0·5 to 1 ml. portion being added dropwise. The method is accurate to 0·06 per cent. Full experimental details are given in *Procedure B* below.

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* For further experimental details and an account of the numerous applications of this method, the reader is referred to W. Bottger-R. E. Oesper, *Newer Methods of Volumetric Chemical Analysis*, 1938, p. 55. (D. Van Nostrand ; Chapman and Hall.)

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \\ = MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

The procedure of H. A. Bright (1937), which utilises arsenious oxide as a primary standard and potassium iodide or potassium iodate as a catalyst for the reaction, is more convenient in practice and promises to take first place as a trustworthy method for the standardisation of permanganate solutions. Like sodium oxalate, A.R. arsenious oxide has a purity of at least 99·9 per cent, and the U.S. Bureau of Standards supplies a product of 99·98 per cent guaranteed purity.† The results by this method agree to within 1 part in 3000 with the sodium oxalate procedure of Fowler and Bright. Full experimental details are given in *Procedure A.*

$$5As_2O_3 + 4MnO_4^- + 12H^+ = 5As_2O_5 + 4Mn^{++} + 6H_2O ;$$

$$5As_2O_3 + 4KMnO_4 + 12\,HCl \\ = 4MnCl_2 + 4KCl + 5As_2O_5 + 6H_2O$$

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* A.R. sodium oxalate of the Mallinckrodt Chemical Works, U.S.A., has an assay value of 99·95 per cent. The Bureau of Analysed Samples of Middlesbrough, England, supply a " British Chemical Standard " sodium oxalate of 99·94 per cent purity. See also Appendix, Section **A, 9.**

† A.R. arsenious oxide of the Mallinckrodt Chemical Works, U.S.A., has an assay value of 99·95 per cent. See Appendix, Sections **A, 8, 9,**

Iron wire of 99·9 per cent purity is available commercially. The A.R. reagent[*] is a suitable standard, particularly if the potassium permanganate solution is subsequently to be employed in the estimation of iron. If the wire exhibits any sign of rust, it should be drawn between two pieces of fine emery cloth, and then wiped with a clean dry cloth before use. The reaction which occurs is :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \\ = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

The use of crystallised oxalic acid, potassium tetroxalate, and ferrous ammonium sulphate (Mohr's salt) for standardisation is not recommended for accurate work ; they may, however, be employed for elementary students in work in which great accuracy is not required. All these substances are hydrated, and unless special precautions are taken in drying and storage the water content may be open to suspicion. Furthermore, for potassium tetroxalate and Mohr's salt it is difficult to be quite sure that the constituent salts are present in exactly equimolecular proportions. The A.R. substances have the following assay values[†] : $H_2C_2O_4,2H_2O \not< 99·8$ per cent ; $KHC_2O_4,H_2C_2O_4, 2H_2O \not< 99·9$ per cent ; and $FeSO_4,(NH_4)_2SO_4, 6H_2O$ 99·5 to 100·5 per cent. Apart from the objections already mentioned, it is evident that A.R. ferrous ammonium sulphate cannot be used directly for standardisation, even for work of moderate accuracy. It must first be dissolved in warm water, and the solution rapidly cooled to ensure the production of small crystals ; these are filtered at the pump, washed with a little distilled water, repeatedly pressed between sheets of clean filter paper, and placed in a current of air to dry thoroughly. The substance is dry when the small grains no longer adhere to each other or to the paper in which they are contained, and is then preserved in a stoppered bottle for use.

III, 47. Preparation of 0·1*N* potassium permanganate.— Weigh out about 3·2 to 3·25 g. of A.R. potassium permanganate on a watch glass, transfer it to a 1500 ml. beaker, add 1 litre of water, cover the beaker with a clock glass (or Fisher " speedyvap " beaker cover), heat the solution to boiling, boil gently for 15 to 30 minutes, and allow the solution to cool to the laboratory temperature. Filter the solution through a funnel containing a plug of purified glass wool, or through a Gooch crucible provided with a pad of purified asbestos, or, most simply, through a Jena sintered glass filter crucible or funnel. Collect the filtrate in a vessel which has been cleaned with chromic acid mixture and then thoroughly washed with distilled water. The filtered solution should be stored in a clean glass-stoppered bottle, and kept in the dark or in diffuse light except when in use : alternatively, it may be kept in a bottle of dark-brown coloured glass.

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[*] The author has found that the " Iron Wire Analytical Reagent " supplied by the Mallinckrodt Chemical Works, U.S.A., in sealed glass vials to be very satisfactory. The assay value is 99·9 per cent Fe and the percentages of impurities are given on the label. If the vials are carefully resealed with wax after each opening, and care be taken to prevent the introduction of moisture from the hands and other sources, the iron wire retains its original bright surface for long periods.

[†] These figures are taken from *AnalaR Standards for Laboratory Chemicals*, 2nd edition, 1937, published jointly by Hopkin and Williams Ltd., London, and British Drug Houses Ltd., London.

III, 48. Standardisation of permanganate solutions.—*Procedure A.* **With arsenious oxide** (H. A. Bright, 1937). Dry some A.R. arsenious oxide at 105° to 110°C for 1 to 2 hours, and allow to cool in a desiccator. Accurately weigh approximately 0·25 g. of the dry oxide, and transfer it to a 400 ml. beaker. Add 10 ml. of a cool solution of sodium hydroxide, prepared from 20 g. of sodium hydroxide and 100 ml. of water (1). Allow to stand for 8 to 10 minutes, stirring occasionally. When solution is complete, add 100 ml. of water, 10 ml. of pure concentrated hydrochloric acid, and 1 drop of 0·0025M potassium iodide or potassium iodate (2). Add the permanganate solution from a burette until a faint pink colour persists for 30 seconds. Add the last 1 to 1·5 ml. dropwise, allowing each drop to become decolourised before the next drop is introduced. (For the most accurate work it is necessary to determine the volume of permanganate solution required to duplicate the pink colour at the end point. This is done by adding permanganate solution to a solution containing the same amounts of alkali, acid and catalyst as were used in the test. The correction should not be more than 0·03 ml.*) Repeat the determination with two other similar quantities of arsenious oxide. Calculate the normality of the potassium permanganate solution. Duplicate determinations should agree within 0·1 per cent.

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* The end point can also be determined with tri-ortho-phenanthroline ferrous sulphate as indicator. As the end point is approached one drop of the indicator (Section **III, 63**) is added. The permanganate solution is then added dropwise until the pink colour of the indicator changes to a very faint blue. The blank correction should average about 0·02 ml.

Notes. 1. For *elementary students*, it is sufficient to weigh out accurately about 1·25 g. of A.R. arsenious oxide, dissolve this in 50 ml. of a cool 20 per cent solution of sodium hydroxide, and make up to 250 ml. in a volumetric flask. Shake well. Remove 25 ml. of this solution by means of a burette and **not** with a pipette (**caution—the solution is highly poisonous**), transfer to a 250 to 350 ml. conical flask, add 100 ml. of water, 10 ml. of pure concentrated hydrochloric acid, 1 drop of potassium iodide solution, and titrated with the permanganate solution to the first permanent pink colour as detailed above. Repeat with two other 25 ml. portions of the solution. Successive titrations should agree within 0·1 ml.

2. 0·0025*M* potassium iodide = 0·41 g. KI per litre ; 0·0025*M* potassium iodate = 0·54 g. KIO_3 per litre.

Calculation. It is evident from the equation given in Section **III, 46** and also from the equation

$$As_2O_3 + 2O = As_2O_5$$

that the equivalent weight of arsenious oxide is one quarter of the molecular weight, 197·82/4 or 49·46 g. 1 Ml. of a normal solution contains the milli-equivalent weight, or 0·04946 g. If the weight of arsenious oxide be divided by the number of ml. of potassium permanganate solution to which it is equivalent as found by titration, we have the weight of primary standard equivalent to 1 ml. of the permanganate solution. If this last value be divided by the milli-equivalent of arsenious oxide, the normality of the permanganate solution is obtained (for details of an actual calculation, see under Sodium Carbonate, Section **III, 4A**).

In the method described in *Note 1*, the normality of the arsenious oxide solution is calculated from the weight of arsenious oxide used (1 litre of a *N* solution contains 49·46 g. of As_2O_3). The normality of the permanganate solution is then computed from the relation :

$$V_A \times n_A = V_B \times n_B$$

(compare Section **III, 4A**).

Procedure B. **With sodium oxalate** (R. M. Fowler and H. A. Bright, 1935). Dry some A.R. sodium oxalate at 105° to 110°C for 2 hours, and allow it to cool in a desiccator. Weigh out accurately from a weighing bottle about 0·3 g. of the dry sodium oxalate into a 600 ml. beaker, add 240 ml. of water, and 12·5 ml. of concentrated sulphuric acid (*caution*)*.

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* Or 250 ml. of approximately 2*N* sulphuric acid, prepared by adding 50 ml. of concentrated sulphuric acid cautiously to 950 ml. of water.

Cool to 25° to 30°C, and stir until the oxalate has dissolved (1). Add 90 to 95 per cent of the required quantity of permanganate solution from a burette at a rate of 25 to 35 ml. per minute while stirring slowly (2). Heat to 55° to 60°C (use a thermometer as stirring rod), and complete the titration by adding permanganate solution until a faint pink colour persists for 30 seconds. Add the last 0·5 to 1 ml. dropwise with particular care to allow each drop to become decolourised before the next is introduced. (For the most exact work, it is necessary to determine the excess of permanganate solution required to impart a pink colour to the solution. This is done by matching the colour produced by adding permanganate solution to the same volume of boiled and cooled diluted sulphuric acid at 55° to 60°C. This correction usually amounts to 0·03 to 0·05 ml.) Repeat the determination with two other similar quantities of sodium oxalate.

Calculate the normality of the potassium permanganate solution. Duplicate determinations should agree within 0·1 to 0·2 per cent.

Notes. 1. For *elementary students*, it is sufficient to weigh out accurately about 1·7 g. of A.R. sodium oxalate, transfer it to a 250 ml. volumetric flask, and make up to the mark. Shake well. Use 25 ml. of this solution per titration and add 150 ml. of *ca.* 2*N* sulphuric acid. Carry out the titration rapidly at the ordinary temperature until the *first* pink colour appears throughout the solution, and allow to stand until the solution is colourless. Warm the solution to 50° to 60°C and continue the titration to a permanent faint pink colour. It must be remembered that oxalate solutions attack glass, so that the solution should not be stored more than a few days.

2. An approximate value of the volume of permanganate solution required can be computed from the weight of sodium oxalate employed. In the first titration about 75 per cent of this volume is added, and the determination is completed at 55° to 60°C. Thereafter, about 90 to 95 per cent of the volume of permanganate solution is added at the laboratory temperature.

Calculation. This is similar to that described under *Procedure A*. The equivalent weight of sodium oxalate is 1/2 mol, or 67·01 g. $KMnO_4$

1 Ml. N $Na_2C_2O_4 \equiv$ 0·06701 g. $Na_2C_2O_4$.

Procedure C. **With metallic iron.** Use A.R. iron wire of 99·9 per cent assay value (see last but one footnote in Section **III, 46**). Fit a tight rubber stopper with a bent delivery tube into a 350 ml. conical flask and clamp it in a retort stand in an inclined position, the tube being bent so as to dip into a small beaker containing saturated sodium bicarbonate solution or 20 per cent potassium bicarbonate solution (prepared from the A.R. solids) (Fig. 3-4). Place 100 ml. of $3N$ sulphuric acid (from 92 ml. of water and 8 ml. of concentrated sulphuric acid) in the flask, and add 0·5 to 1 g. of A.R. sodium bicarbonate in two portions ; the carbon dioxide produced will drive out the air. Meanwhile, weigh out accurately about 0·15 g. of the iron wire, place it quickly into the flask, replace the stopper and bent tube, and warm gently until the iron has dissolved completely. Cool the flask rapidly under a stream of cold water,* and then run in the permanganate solution cautiously from a burette, with constant shaking, until the faint pink colour is permanent. The addition of about 5 ml. of pure syrupy phosphoric acid facilitates the detection of the end point. Repeat the determination with two other samples of the iron wire.

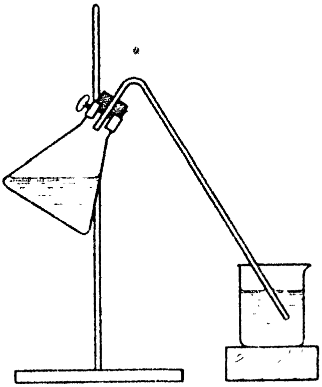

FIG. 3-4.

The reaction is :

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Calculation. The weight of iron wire taken, multiplied by 0·999, will give the weight of pure iron used in each titration.

$$1 \text{ Ml. } N\ KMnO_4 \equiv 0{\cdot}05584 \text{ g. Fe.}$$

Procedure D. **With ferrous ammonium sulphate.** Weigh out accurately about 9·8 g. of the A.R. salt : this should preferably be recrystallised as detailed in Section **III, 46.** Transfer to a 250 ml. volumetric flask, add 200 ml. of water and 5 ml. of concentrated sulphuric acid (or 200 ml. of N sulphuric acid). Shake until the solid has dissolved and make up to the mark with distilled water. Shake well. Remove 25 ml. of the solution with a pipette, add 25 ml. of N sulphuric acid, and titrate with the permanganate solution to the first permanent pink colour. Here also the addition of a few ml. of syrupy phosphoric acid improves the colour change at the end point. Carry out 2 or at most 3 titrations. These should not differ by more than 0·1 ml.

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* As the flask cools, the solution is automatically drawn in until the pressure of the carbon dioxide inside the flask is equal to the atmospheric pressure.

Calculation. The equivalent weight of ferrous ammonium sulphate in this reaction is the molecular weight or 392·13 ($2FeO + O = Fe_2O_3$). Compute the normality of the potassium permanganate solution from the relation:

$$V_A \times n_A = V_B \times n_B$$

(Section **I, 24**).

Procedure E. **With oxalic acid or potassium tetroxalate.** Weigh out accurately either about 1·6 g. of A.R. $H_2C_2O_4,2H_2O$ or about 1·6 g. of A.R. $KHC_2O_4,H_2C_2O_4,2H_2O$, and make up to 250 ml. in a volumetric flask. Shake well. Remove 25 ml. portions with a pipette, add 150 ml. of *ca.* 2*N* sulphuric acid, and titrate against the permanganate solution as detailed under *Procedure B* (sodium oxalate). Successive titrations should agree within 0·1 ml.

Calculation. The partial equation for both reactions is:

$$C_2O_4^{--} + 2\epsilon = 2CO_2,$$

hence the equivalent weight of $H_2C_2O_4,2H_2O$ is 0·5 mol or 63·03, and that for $KHC_2O_4,H_2C_2O_4,2H_2O$ is 0·25 mol or 63·55. Calculate the normality of the potassium permanganate solution as already detailed.

III, 49. Permanence of potassium permanganate solutions. —A *pure* permanganate solution, provided it is kept free from dust, organic matter, precipitated manganese dioxide and reducing vapours, will keep for a long time. For very accurate work, however, it is advisable to standardise the solution frequently, preferably with arsenious oxide. If filtered solutions of permanganate are to be diluted, it is best to use water which has been redistilled from alkaline permanganate, *e.g.*, conductivity water (Section **II, 10C**). The addition of 10 g. of potassium hydroxide per litre increases the stability of the solution.

The student is reminded that owing to the decomposition of permanganate solution by organic matter of any kind, it cannot be filtered through filter paper, nor can it be used in a clip burette because it is decomposed by the india-rubber tube. Filtration is carried out through purified glass wool, asbestos or a sintered glass funnel.

ANALYSES INVOLVING THE USE OF STANDARD POTASSIUM PERMANGANATE SOLUTIONS

III, 50. Determination of ferrous iron.—The detailed experimental method has already been given under *Procedures C* and *D* of Section **III, 48**; the solution is acidified with dilute sulphuric acid. If chloride ion is present high results are obtained, because the reaction between ferrous iron and permanganate induces the oxidation of hydrochloric acid to chlorine (or to hypochlorous acid). The chloride ion is rendered almost harmless by the addition of a manganous salt, preferably in the form of the so-called Zimmermann-Reinhardt solution (Section **III, 46**), and by slow titration.

As an exercise, the student should determine the percentage of iron in crystallised ferrous sulphate, $FeSO_4,7H_2O$. Weigh out accurately about 7 g. of ferrous sulphate crystals, dissolve in 200 ml. of *N* sulphuric acid (195 ml. of water and 5 ml. of concentrated sulphuric acid) in a 250 ml. volumetric flask, and make up to the mark with distilled water. Shake well. Remove 25 ml. of the solution with a pipette into a 250 ml. conical flask, add 25 ml. of *N* sulphuric acid, and titrate with standard 0·1*N* potassium permanganate to the first permanent faint pink colour. Repeat with two other 25 ml. portions of the ferrous solution. Successive titrations should agree within 0·1 ml.

Calculate the percentage of ferrous iron in the crystals.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$
$$1 \text{ Ml. } N\ KMnO_4 \equiv 0{\cdot}05884 \text{ g. Fe.}$$

III, 51. Reduction of ferric to ferrous iron.—Iron often occurs in the ferric state, or as a mixture of ferrous and ferric iron in ores and other materials. For the volumetric determination of iron, the ferric iron must first be quantitatively reduced to the ferrous state. The following methods, in decreasing order of importance and application, are available; (**A**) with stannous chloride; (**B**) with amalgamated zinc or cadmium, preferably in the Jones reductor; (**C**) with titanous salts; (**D**) with sulphurous acid; (**E**) with hydrogen sulphide; and (**F**) with zinc or magnesium and dilute sulphuric acid. Methods **A** and **B** are widely used. Method **C** is described in Section **III, 86.** Method **F** has been largely displaced by **B.**

A. Reduction with stannous chloride solution. Many iron ores are brought into solution with concentrated hydrochloric acid. In such cases the reducing agent frequently employed is stannous chloride :

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The hot iron solution (70° to 90°C), from about 0·3 g. of iron ore, which should occupy a volume of 25 to 30 ml.* and be 5 to 6N with respect to hydrochloric acid, is reduced by adding concentrated stannous chloride solution dropwise from a separating funnel or a burette, with stirring, until the yellow colour of the solution has *nearly* disappeared. The reduction is then completed by diluting the concentrated solution of stannous chloride with 2 volumes of dilute hydrochloric acid, and adding the dilute solution dropwise, with agitation after each addition, until the liquid has a faint green colour, quite free from any tinge of yellow. The solution is then rapidly cooled under the tap, with protection from the air, and the slight excess of stannous chloride present removed by adding 10 ml. of a saturated solution (*ca.* 5 per cent) of mercuric chloride rapidly in one portion. A *slight* silky white precipitate of mercurous chloride should be obtained :

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

The oxidising agent has no appreciable effect upon the small amount of mercurous chloride in suspension. If a heavy precipitate forms or a grey or black precipitate is obtained, too much stannous chloride has been used ; the results are inaccurate and the reduction must be repeated. Finely divided mercury is oxidised by potassium permanganate (and by potassium dichromate).

After the addition of the mercuric chloride solution, the whole is allowed to stand 5 minutes, and transferred quantitatively to a 600 ml. beaker or casserole with the aid of about 400 ml. of water. 25 Ml. of the Zimmermann-Reinhardt solution (the so-called " preventive solution ") are added, and the mixture titrated slowly and with constant stirring with standard 0·1N potassium permanganate. The end point is not the permanent pink colour which is obtained in the absence of a chloride, but is the first pink colouration seen throughout the whole solution ; this colouration fades after about 15 seconds. The fading is due to the reaction between the permanganate solution and the mercurous chloride, and also to the following reaction, which is, however, very slow in cold acid solution :

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* If the volume is greater than this, it must be reduced by careful evaporation

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Blank runs on the reagents should be carried through all the operations, and corrections made, if necessary.

The **concentrated solution of stannous chloride** is prepared by dissolving 12 g. of pure tin or 30 g. of A.R. crystallised stannous chloride ($SnCl_2$, $2H_2O$) in 100 ml. of concentrated hydrochloric acid and diluting to 200 ml. with water.

Details of the Zimmermann-Reinhardt solution are given in Section **III, 46.**

B. Reduction with amalgamated zinc or cadmium. The Jones reductor. Both amalgamated zinc and cadmium are excellent reducing agents for ferric iron :

$$2\,Fe^{+++} + Zn = 2Fe^{++} + Zn^{++}.$$

The former is generally employed. Zinc can be purchased in the pure state : A.R. granulated zinc contains less than 0·002 per cent of iron. Both pure cadmium and zinc react rather slowly with acids, but upon treatment with a dilute solution of a mercuric salt, the metal is covered with a thin layer of mercury ; the amalgamated metal reacts quite readily. Reduction with amalgamated zinc is usually carried out in the "**reductor**", due to C. Jones (1888–1889). This consists of a column of amalgamated zinc contained in a long glass tube provided with a stop-cock, through which the solution to be reduced may be drawn. A large surface is exposed, and consequently such a zinc column is much more efficient than pieces of zinc placed in the solution.

A suitable form of the Jones reductor, with approximate dimensions, is shown in Fig. 3-5. A perforated porcelain plate, covered with purified asbestos or glass wool, supports the zinc column. The tube below the tap passes through a tightly-fitting one-holed rubber stopper into a 750 ml. filter flask.

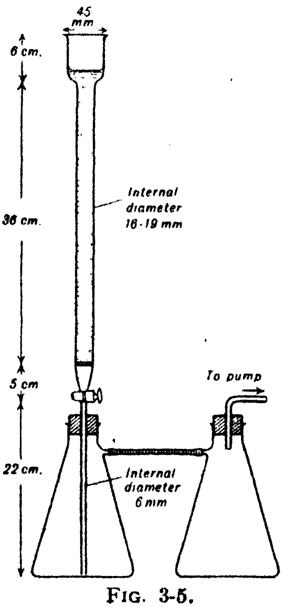

FIG. 3-5.

It is advisable to connect another filter flask in series with the water pump, so that if any water " sucks back " it will not spoil the determination. The amalgamated zinc is prepared as follows. About 300 g. of A.R. granulated zinc (or zinc shavings, or pure 20 to 30 mesh zinc) are covered with 2 per cent mercuric chloride solution in a beaker. The mixture is stirred for 5 to 10 minutes, then the solution is decanted from the zinc, and washed three times with water by decantation. The resultant amalgamated zinc should have a bright silvery lustre. The porcelain plate is placed in position, covered with a layer of purified asbestos or glass wool, and then the amalgamated zinc added ; the latter should reach to the shoulder of the tube. The zinc is washed with distilled water (500 ml.), using gentle suction. If the reductor is not to be used immediately, it must be left full of water in order to prevent the formation of basic salts by atmospheric oxidation, which impair the reducing surface.

To use the reductor for the reduction of ferric iron, proceed as follows. The zinc is activated by filling the cup (which holds about 50 ml.) with $2N$ (*ca.* 5 per cent) sulphuric acid, the tap being closed. The flask is connected to a filter pump, the tap opened, and the acid *slowly* drawn through the column until it has fallen *just above the level of the zinc* ; the tap is then closed and the process repeated twice. The tap is shut, the flask detached, cleaned and replaced. The reductor is now ready for use. It is important to note that during use the level of the liquid should always be just above the top of the zinc column. The solution to be reduced should have a volume of 100 to 150 ml., contain not more than 0·25 g. of iron, and be about $2N$ in sulphuric acid. The cold ferric iron solution is passed through the reductor, using gentle suction, at a rate not exceeding 75 to 100 ml. per minute. As soon as the reservoir is nearly emptied of the solution, 100 ml. of 2·5 per cent sulphuric acid is passed through in two portions, followed by 100 to 150 ml. of water. The last washing is necessary in order to wash out all of the reduced compound and also the acid, which would otherwise cause unnecessary consumption of the zinc. Disconnect the flask from the reductor, wash the end of the delivery tube, and titrate immediately with standard $0{\cdot}1N$ potassium permanganate.

Carry out a blank determination, preferably before passing the iron solution through the reductor, by running the same volumes of acid and water through the apparatus as are used in the actual determination. This should not amount to more than about 0·1 ml. of 0·1*N* permanganate, and should be deducted from the volume of permanganate solution used in the subsequent titration.

It must be emphasised that if hydrochloric acid has been employed in the original solution of the iron-bearing material, the volume should be reduced to *ca.* 25 ml. and then diluted to *ca.* 150 ml. with 5 per cent sulphuric acid. The estimation is carried out as detailed above, but 25 ml. of the Zimmermann-Reinhardt solution must be added before titration with the standard potassium permanganate solution. A better method is to expel the hydrochloric acid by careful evaporation with an excess of sulphuric acid before the solution is reduced ; the addition of the Zimmermann-Reinhardt solution is then unnecessary, and the end point is more stable.

Applications and limitations of the Jones reductor.

1. Solutions containing 1 to 10 per cent by volume of sulphuric acid or 3 to 15 per cent by volume of concentrated hydrochloric acid can be used in the reductor. If permanganate solution is to be used later, hydrochloric acid is best avoided.

2. Nitric acid must be absent, for this is reduced to hydroxylamine and other compounds which react with permanganate. If nitric acid is present, evaporate the solution just to dryness, wash the sides of the vessel with about 3 ml. of water, carefully add 3 to 4 ml. of concentrated sulphuric acid, and evaporate until fumes of the latter are evolved. Repeat this operation twice to ensure complete removal of the nitric acid, dilute to 100 ml. with water, add 5 ml. of concentrated sulphuric acid, and proceed with the reduction.

3. Organic matter (acetates, etc.) must be absent. It is removed by heating to fumes of sulphuric acid in a covered beaker (best with a cover of the Fisher " speedyvap" type), then carefully adding drops of a saturated solution of potassium permanganate until a permanent colour is obtained, and finally continuing the fuming for a few minutes.

4. Solutions containing compounds of copper, tin, arsenic, antimony and other reducible metals must never be used. These must be removed before the reduction by treatment with hydrogen sulphide.

5. Other elements which are reduced in the reductor to a definite valency stage are titanium to Ti^{+++}, chromium to Cr^{++}, molybdenum to Mo^{+++} and vanadium to V^{++}. Uranium is reduced to slightly below the quadrivalent state, but by bubbling a stream of air through the solution in the filter flask for a few minutes, the dirty dark green colour changes to the bright apple-green colour characteristic of pure uranous salts U^{++++}. Tungsten and niobium are reduced, but not to any definite valency state.

With the exception of ferrous iron and quadrivalent uranium, the reduced solutions are extremely unstable and readily re-oxidise upon exposure to air. These are best caught in a five-fold excess of a solution of ferric alum (150 g. of A.R. iron alum and 150 ml. of concentrated sulphuric acid per litre ; approximately 0·3N with respect to iron) contained in the filter flask. The ferrous iron formed is then titrated with a standard solution of a suitable oxidising agent. Titanium and chromium are completely oxidised and liberate an equivalent amount of ferrous sulphate ; molybdenum is re-oxidised to the quinquevalent (red) stage, which is fairly stable in air, and complete oxidation is effected by the permanganate, but the net result is the same, *viz.*, $Mo^{III} \rightarrow Mo^{VI}$; vanadium is re-oxidised to the quadrivalent condition, which is stable in air, and the final oxidation is completed by slow titration with potassium permanganate solution.

D. Reduction with sulphurous acid. The solution must be feebly acid and fairly dilute, say, 500 ml. for 0·5 g. of iron. If the concentration of the acid exceeds 5N, sulphurous acid will oxidise ferrous solutions. Hydrochloric acid-chloride solutions are reduced more rapidly than sulphuric acid-sulphate solutions. Either sulphur dioxide from a siphon of the liquid gas or *freshly prepared* sulphurous acid solution or ammonium bisulphite solution may be used. The operation is best carried out in an all-glass special wash bottle or, if this is not available, in a flask fitted with a rubber stopper carrying two " wash bottle " tubes.

Treat the hydrochloric acid or sulphuric acid solution of the iron slowly and with constant shaking with dilute ammonia solution until a faint permanent precipitate is obtained. Dilute to about 100 ml., pass sulphur dioxide through the solution for 2 to 3 minutes, and then gradually heat to boiling, still continuing the passage of the gas. When the solution is colourless (15 to 30 minutes), replace the sulphur dioxide by a stream of washed carbon dioxide (from a Kipp's apparatus or cylinder), and boil vigorously until all the sulphur dioxide is expelled (20 to 30 minutes) as shown by passing the escaping gas for 30 seconds through dilute sulphuric acid containing

2 drops of 0·1*N* permanganate. Allow the solution to c in a stream of carbon dioxide, add more acid, and titrate a standard solution of a suitable oxidising agent.

A simpler method is to place the acidified iron solution in a conical flask, add dilute ammonia solution slowly until a faint permanent precipitate is obtained, and then add either 25 ml. of a freshly prepared saturated solution of sulphur dioxide or excess of freshly prepared ammonium bisulphite solution ; in the latter case, boiling water followed by a little dilute sulphuric acid is added. A small funnel is placed in the mouth of the flask, and the mixture boiled for 30 minutes. All the sulphur dioxide will then have been expelled. Cool the solution in an atmosphere of carbon dioxide, add 10 ml. of dilute sulphuric acid (1 : 6), and titrate at once with a standard solution of the oxidising agent.

Members of the hydrogen sulphide group of metals must be absent. If present, they must be removed first.

E. Reduction with hydrogen sulphide. This method is not frequently employed. The best experimental conditions are as follows. About 100 ml. of a cold 2·5 per cent sulphuric acid solution of the iron compound is treated with a current of washed hydrogen sulphide for 30 minutes, and then for a further 15 minutes during which the solution is heated to boiling. 15 Ml. of sulphuric acid (1 : 1) are added, and the solution is boiled down to about 50 ml. during 30 to 60 minutes whilst a stream of oxygen-free carbon dioxide is passed through. The solution is allowed to cool in a stream of the gas, diluted to 200 ml. with distilled water, and titrated with standard permanganate solution. The precipitated sulphur is coagulated during the concentration, and usually need not be removed before titration. The results are slightly high.

F. Reduction with zinc and sulphuric acid. This method has been largely replaced by that employing amalgamated zinc, but is given here for the sake of completeness. The solution to be reduced should be dilute (*e.g.*, not more than 0·15 g. of iron per 200 ml. ; for this quantity about 10 g. of zinc and 25 ml. of sulphuric acid are necessary). Place 15 ml. of the iron solution in a 350 ml. conical or flat-botto flask, add cautiously 20 ml. of concentrated sulphuric acid and 10 g. of A.R. zinc. The reaction will usually be slow, and is accelerated by the addition of two to three drops of copper sulphate solution. Warm very gently and allow the reaction to continue until the solution appears quite colourless or pale green) : a short funnel should be placed in the neck the flask to prevent loss by spray. Test for the presence erric salt by removing a drop of the solution on the end of a thin glass rod, or at the end of a capillary tube, and bringing it into contact with a drop of potassium or ammonium thiocyanate solution upon a porcelain " spot " plate. No red colour should appear, or at most only a faint pink tint, if all the ferric iron has been reduced ; otherwise a red colouration is formed. When all the iron has been reduced, close the flask by means of a one-holed rubber stopper carrying a Bunsen valve (Fig. 3-6), and boil the mixture gently until all the zinc has dissolved. (A *Bunsen valve* consists of a piece of glass tubing carrying a short length of rubber tubing, which is closed at the upper end by a short glass rod. The rubber tube has a vertical slit, about 1 to 2 cm. long, forming the valve ; this allows gas or vapour to pass out, but is closed by atmospheric pressure when the evolution ceases, thus preventing the entrance of air.) When the zinc has completely dissolved, allow the solution to cool, remove the stopper, and titrate the contents of the flask with standard permanganate solution.

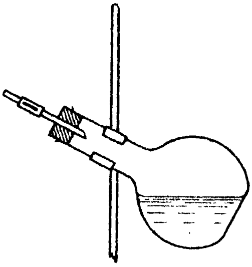

Fig. 3-6.

For reduction with liquid zinc amalgam, see Section **III, 90.**

III, 52. Determination of iron in ferric ammonium sulphate.—In order to obtain experience in the various methods of reduction described in the preceding Section, the student is recommended to estimate the percentage of iron in ferric alum, $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$. It is best to employ the A.R. material, as some check can be made by calculation upon the accuracy of the result obtained.

Weigh out accurately about 24 g. of A.R. ferric alum, transfer it to a 500 ml. volumetric flask, dissolve it in water containing about 100 ml. of dilute sulphuric acid (2*N* ; *ca.* 5 per nt), and make up to the mark with water. Shake well. uce the iron in 25 ml. portions (i) by the stannous chloride method, (ii) by the sulphurous acid method, and (iii) by the Jones reductor, if available. In all cases the final solution should be titrated against standard 0·1*N* potassium permanganate. Individual determinations should agree within 0·1 ml. of the permanganate solution.

Calculate the percentage of iron in the compound fo
method of reduction.

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}05884 \text{ g. Fe.}$$

The volume of permanganate solution used is multipli
its normality ; this gives the volume of *N* solution to whic
is equivalent. If the latter volume is multiplied by the milli-equivalent of iron (0·05884 g.), the weight of iron in the volume of solution titrated is obtained, from which the percentage of iron is readily calculated.

III, 53. Determination of the total iron in an iron ore.—For practice, the student may employ either spathic iron ore (largely ferrous carbonate)* or the iron ore supplied by the instructor. Weigh out accurately about 2 g. of the finely-ground ore and dissolve it in 100 ml. of dilute hydrochloric acid (1 : 1) in a conical flask carrying a short funnel in the neck. Warm gently, and continue the heating until the residue is free from coloured material. Rinse down the funnel and the neck of the flask with distilled water, cool, and filter the liquid through a hardened quantitative filter paper into a 250 ml. volumetric flask. Wash with very dilute hydrochloric acid and allow the washings to pass into the flask. Remove the funnel and make up to the mark. Shake well. Remove 50 ml. of the liquid by means of a pipette to a conical flask, heat to boiling, and reduce the ferric salt by the stannous chloride method (Section **III, 51 A**). Pour the reduced solution into 400 ml. of water containing 25 ml. of the Zimmermann-Reinhardt solution (Section **III, 46**), and titrate slowly with standard $0{\cdot}1N$ potassium permanganate to the first pink colour which is stable for 15 seconds. Repeat the titration with two other 50 ml. portions of the solution.

Calculate the percentage of iron in the iron ore.

III, 54. Determination of calcium in calcium carbonate.—*Discussion.* Metals, such as calcium, copper, lead and zinc, which give slightly soluble oxalates may be determined by dissolving the washed precipitate in dilute sulphuric acid and titrating with standard permanganate solution. The method is widely used for the estimation of calcium., The calcium is precipitated as the oxalate by the addition of ammonium oxalate solution to a dilute hydrochloric acid solution of the element, followed by neutralisation of the acid with dilute a solution. The washed precipitate is dissolved in lphuric acid, and the liberated oxalic acid titrated dard permanganate solution.

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* Suitable iron ores are Ridsdale's " Iron Ore, No. 17 " (one of the Analysed Samples for Students) and " Iron Ore ' A ' " (a British Chemical Standard) of the Bureau of Analysed Samples.

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4;$$

$$nO_4 + 3H_2SO_4 + 5H_2C_2O_4$$
$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

It must be pointed out that the above method is not quite satisfactory for the determination of lead, because of the formation of a coating of lead sulphate over the lead oxalate. In this case the following procedure, which can be applied to all the elements given above, should be used. The oxalate of the metal is precipitated by a known excess of oxalic acid or ammonium oxalate solution in the presence of ammonia solution (details are given below), the precipitate is filtered and well washed, and the excess of oxalate in the filtrate and washings determined by titration with standard potassium permanganate solution in the usual manner.

Procedure. Weigh out accurately 0·15 to 0·2 g. of calcium carbonate, preferably of A.R. grade, into a 400 ml. beaker. Add 20 ml. of water and cover the beaker with a clock glass. Add 10 ml. of dilute hydrochloric acid (1 : 1) and warm until the solid has dissolved. Rinse the sides of the vessel and the clock glass, dilute to 200 ml., and add a few drops of methyl red indicator. Heat the solution to boiling, and add a clear solution of 1·5 g. of ammonium oxalate dissolved in 25 ml. of water slowly and with constant stirring ; some calcium oxalate may be precipitated in the acid solution owing to the large excess used. To the hot solution (70° to 80°C) add dilute ammonia solution (1 : 1) dropwise and with stirring from a burette until the liquid is neutral or faintly alkaline (colour change from red to yellow). Allow the solution to stand for an hour in a warm place. Decant the clear supernatant liquid through a Whatman No. 40 or No. 540 filter paper ; test the filtrate for the presence of calcium with ammonium oxalate. Transfer the precipitate quantitatively to the filter (Section **II, 28**), and wash the precipitate on the filter repeatedly with small quantities of cold water until the washings are oxalate and chloride-free. Pierce a hole in the filter with a pointed glass rod, and wash the bulk of the precipitate through the funnel into a conical flask with hot water. Treat the filter with small quantities of dilute sulphuric acid (1 : 8), and again wash into the flask. Finally wash the filter paper thoroughly with hot water. When the precipitate has completely dissolved (add more dilute sulphuric acid, if necessary), dilute the solution to about 200 ml., and titrate with standard 0·1N potassium permanganate (for details, see Section **III, 48,** *Procedure B*).

The calcium oxalate precipitate may also be filtered through a sintered glass or porous porcelain crucible. The precipitate is then washed with dilute sulphuric acid (5 per cent) until dissolved. The sulphuric acid is added in small portions and is allowed to remain in contact with the precipitate before being drawn into the suction flask. The solution in the flask is diluted and titrated with standard 0·1N permanganate.

Repeat the determination with two other samples of the calcium carbonate.

Calculate the percentage of calcium in the calcium carbonate.

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}02004 \text{ g. Ca} \equiv 0{\cdot}02804 \text{ g. CaO.}$$

III, 55. Analysis of hydrogen peroxide.—*Discussion.* Hydrogen peroxide is marketed in four concentrations, " 10," " 20," " 40 " and " 100 volume " concentrations. The " 10 volume " solution refers to the fact that the solution, when fully decomposed by heat, yields 10 times its volume of oxygen measured at 0°C and 760 mm.

$$\underset{2\times 34{\cdot}02 \text{ g.}}{2H_2O_2} = 2H_2O + \underset{22{\cdot}4 \text{ litres (at N.T.P.)}}{O_2}.$$

A " 10 volume " preparation should contain about 3 per cent H_2O_2. The following reaction occurs when potassium permanganate solution is added to hydrogen peroxide solution acidified with dilute sulphuric acid :

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

This forms the basis of the following method of analysis.

Procedure. Transfer 25 ml. of the " 10 volume " solution by means of a burette (1) to a 250 ml. measuring flask, and dilute with water to the mark. Shake thoroughly. Transfer 25 ml. of this solution to a conical flask, dilute with 200 ml. of water, add 20 ml. of dilute sulphuric acid (1 : 5), and titrate with standard 0·1N potassium permanganate to the first permanent, faint pink colour. Repeat the titration ; two consecutive determinations should agree within 0·1 ml.

Calculate (i) the weight of hydrogen peroxide per litre of the original solution and (ii) the " volume strength," *i.e.*, the number of ml. of oxygen at N.T.P. that can be obtained from 1 ml. of the original solution.

1 Ml. N $KMnO_4 \equiv 0{\cdot}01701$ g. H_2O_2.

Note. 1. If the percentage is required by weight, the specific gravity of the original solution may be taken as unity. A better procedure is to weigh out the original sample in a weighing bottle.

III, 56. Analysis of sodium peroxide.—In this analysis, precautions must be taken to prevent loss of active oxygen. Prepare a cold mixture of 100 ml of water, 5 ml. of concentrated sulphuric acid, and 5 g. of pure boric acid.* Transfer gradually about 0·5 g. of the sodium peroxide from a weighing bottle to the mixture, which is kept vigorously stirred. Make up the solution to 250 ml. in a measuring flask, and shake well. Titrate 50 ml. portions of this solution with standard 0·1N potassium permanganate.

Calculate the percentage purity of the sample.

1 Ml. N $KMnO_4 \equiv 0{\cdot}03900$ g. Na_2O_2.

Note. Barium peroxide may be evaluated by dissolving a weighed quantity (say 1 g.) in 200 ml. of N hydrochloric acid, and making up to 250 ml. in a volumetric flask. 50 Ml. portions are titrated with standard 0·1N potassium permanganate.

1 Ml. N $KMnO_4 = 0{\cdot}08468$ g. BaO_2.

The use of the Zimmermann and Reinhardt's solution is not necessary in this case (compare Section **III, 46**).

III, 57. Determination of manganese dioxide in pyrolusite.—*Discussion.* Manganese dioxide occurs in nature as the mineral pyrolusite. For many purposes, a knowledge of the percentage of MnO_2 is required. This may be determined by treatment with an excess of an acidified solution of a reducing agent, such as ferrous sulphate, sodium oxalate or arsenious oxide.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$$
$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$
$$2MnO_2 + As_2O_3 + 2H_2SO_4 = 2MnSO_4 + As_2O_5 + 2H_2O.$$

The excess of reducing agent is determined by titration with standard permanganate solution. The disadvantage of using ferrous sulphate solution is that the operation must be carried out in an atmosphere free from air (*e.g.*, carbon dioxide) in order to prevent the aerial oxidation of the ferrous salt. Both sodium oxalate and arsenious oxide, which are primary standards and are stable in air, are more convenient. Arsenious oxide is somewhat more trustworthy in this estimation than is sodium oxalate, because oxalic acid decomposes very slowly at high temperatures into carbon monoxide and carbon dioxide, the decomposition being catalysed by manganous salts; the extent of decomposition under ordinary circumstances is, however, very small. Both procedures will be described.

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* This is added in order that the relatively stable "perboric acid" may be formed upon the addition of the sodium peroxide.

Procedure A (**arsenious oxide method**). Dry the finely-powdered sample of pyrolusite at 120°C to constant weight. Weigh out accurately from a weighing bottle about 0·2 g. of the sample into a 250 ml. conical flask, add 50 ml. of standard 0·1N arsenious oxide (Section **III, 48A,** *Note 1*) and 10 ml. of concentrated sulphuric acid. Place a short funnel in the mouth of the flask, and boil until the pyrolusite has decomposed completely; no brown or black particles should then be present. Cool the solution, add 1 drop of 0·0025M potassium iodide solution, and titrate the excess of arsenious oxide with standard 0·1N potassium permanganate. Repeat the determination with two other samples of the solid.

Calculate the percentage of MnO_2 in the pyrolusite from the amount of arsenious oxide consumed in the titration.

$$1 \text{ Ml. } N\ KMnO_4 \equiv 1 \text{ ml. } N\ As_2O_3 \equiv 0{\cdot}04346 \text{ g. } MnO_2.$$

Procedure B (**sodium oxalate method**). Weigh out accurately about 0·2 g. of the finely-powdered, dry pyrolusite into a conical flask, add 50 ml. of standard 0·1N sodium oxalate (Section **III, 48B,** *Note 1*), add 50 ml. of 4N sulphuric acid (*ca.* 10 per cent), and place a short funnel in the mouth of the flask. Boil the mixture gently until no black particles remain. Allow to cool, and titrate the excess of oxalate with standard 0·1N potassium permanganate as detailed in Section **III, 48**, *Procedure B*. Repeat the determination with two other samples of similar weight.

Calculate the amount of sodium oxalate consumed in the reaction, and from this the percentage of MnO_2 in the pyrolusite.

$$1 \text{ Ml. } N\ KMnO_4 \equiv 1 \text{ ml. } N\ Na_2C_2O_4 \equiv 0{\cdot}04346 \text{ g. } MnO_2.$$

Note on the analysis of red lead. A weighed quantity (about 0·3 g.) of red lead is heated with about 30 ml. of 2N nitric acid. The following reaction occurs:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

When the reaction is over, 50 ml. of 0·1*N* sodium oxalate is added, and the mixture boiled until the solution is almost clear and colourless. The excess of the oxalate is then titrated with standard 0·1*N* potassium permanganate.

III, 58. Determination of nitrites.—*Discussion.* Nitrites react in warm acid solution (*ca.* 40°C) with permanganate solution in accordance with the equation :

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

If a solution of a nitrite is titrated in the ordinary way with potassium permanganate, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid. Nitrous acid is liberated, which being volatile and unstable, is partially lost. If, however, a measured volume of standard potassium permanganate solution, acidified with dilute sulphuric acid, is treated with the nitrite solution, added from a burette, until the permanganate is just decolourised, results accurate to 0·5 to 1 per cent may be obtained. This is due to the fact that nitrous acid does not react instantaneously with the permanganate. More accurate results may be secured by adding the nitrite to an acidified solution in which permanganate is present in excess (the tip of the pipette containing the nitrite solution should be below the surface of the liquid during the addition), and back-titrating the potassium permanganate with a solution of ferrous ammonium sulphate, which has recently been compared with the permanganate solution.

For practice in this estimation, the student may determine the purity of commercial potassium nitrite.

Procedure. Weigh out accurately about 1·1 g. of commercial potassium nitrite, dissolve it in cold water, and dilute to 250 ml. in a volumetric flask. Shake well. Measure out 25 ml. of standard 0·1*N* potassium permanganate into a 500 ml. flask, add 300 ml. of 0·75*N* sulphuric acid, and heat to 40°C. Place the nitrite solution in the burette, and add it slowly and with constant stirring until the permanganate solution is just decolourised. Better results are attained by allowing the tip of the burette to dip under the surface of the diluted permanganate solution. Towards the end the reaction is sluggish, so that the nitrite solution must be added very slowly. Repeat the titration with two other 25 ml. portions of the permanganate solution.

Calculate the percentage of KNO_2 in the commercial sample.

1 Ml. N $KMnO_4 \equiv 0{\cdot}02351$ g. $HNO_2 \equiv 0{\cdot}04256$ g. KNO_2.

III, 59. Determination of persulphates.—*Discussion.* Alkali persulphates can readily be evaluated by adding to their solutions a known excess of an acidified ferrous salt solution, and determining the excess of ferrous iron by titration with standard potassium permanganate solution.

$$K_2S_2O_8 + 2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2KHSO_4.$$

For practice, the student may determine the purity of potassium persulphate, preferably of A.R. quality.

Procedure. Prepare an approximately $0{\cdot}1N$ solution of ferrous ammonium sulphate as described in Section **III, 48,** *Procedure D,* and titrate this against standard $0{\cdot}1N$ potassium permanganate. Weigh out accurately about 0·3 g. of potassium persulphate into a conical flask fitted with a Bunsen valve (Fig. 3-6). Remove the rubber stopper carrying the valve, displace the air by carbon dioxide, add 50 ml. of the acidified *ca.* $0{\cdot}1N$ ferrous solution, followed by 150 to 200 ml. of boiling water so as to raise the temperature to at least 80°C. Close the flask and mix the contents thoroughly. When the solid has dissolved, cool the solution by immersion in cold water, and titrate the excess of ferrous iron against standard $0{\cdot}1N$ potassium permanganate. Repeat the titration with two further quantities of the potassium persulphate.

From the difference between the volume of $0{\cdot}1N$ permanganate required to oxidise 50 ml. of the ferrous solution and that required to oxidise the ferrous salt remaining after the addition of the persulphate, calculate the percentage purity of the sample.

1 Ml. N $KMnO_4 \equiv 0{\cdot}1352$ g. $K_2S_2O_8$.

III, 60. Determination of manganese in steel (bismuthate method).—*Discussion.* Sodium bismuthate of commerce is a brown powder of somewhat indefinite composition; the oxidising component is usually taken as $NaBiO_3$. The A.R. product contains about 85 per cent of $NaBiO_3$. Manganous salts are oxidised to permanganic acid by excess of sodium bismuthate in the presence of nitric acid:

$$\begin{aligned}2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \\ = 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O.\end{aligned}$$

The permanganic acid is very stable in a cold solution containing 20 to 40 per cent of nitric acid. If the steel is dissolved in nitric acid and the resultant cold solution treated with excess of sodium bismuthate, permanganic acid is formed. The excess of bismuthate is removed by filtration, and a measured excess of standard ferrous solution added to reduce the permanganate to a manganous salt :

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

The excess of ferrous iron is then determined by titration with standard potassium permanganate solution.

The solution should be free from cobalt, chromium, and chloride.

Procedure. Prepare the following solutions :

0·03*N* Potassium permanganate. Dissolve 1 g. of A.R. potassium permanganate in 1 litre of water (Section **III, 47**).

0·03*N* Ferrous ammonium sulphate. Dissolve 12 g. of A.R. ferrous ammonium sulphate in 1 litre of 5 per cent sulphuric acid (Section **III, 48,** *Procedure D*).

3 Per cent nitric acid free from nitrous acid. Boil concentrated nitric acid (*d* 1·42) for a short time (fume cupboard). Dilute in the proportion of 3 ml. of the concentrated acid to 100 ml. of water. (One ml. of nitric acid, *d* 1·42, contains nearly 1 g. of HNO_3. The above is therefore a 3 per cent solution both by volume and by weight.)

Standardise the permanganate solution against A.R. sodium oxalate either by weighing out accurately about 0·1 g. of the dry oxalate and proceeding as in Section **III, 48** (*Procedure B*) or by preparing an approximately 0·03*N* solution (0·5 g. per 250 ml.) and following the experimental procedure of Section **III, 48,** *Procedure B, Note* 1. Alternatively, the arsenious oxide method (Section **III, 40**, *Procedure A*) may be used.

Weigh out accurately about 1 g. of the sample containing 0·2 to 1 per cent of manganese,* and dissolve it in 50 ml. of dilute nitric acid (1 : 3) in a 250 ml. conical flask. Filter, if necessary, through a sintered glass crucible. Boil for 5 minutes, cool, add 0·5 g. of A.R. sodium bismuthate, and boil again for 5 minutes. A pink colour due to permanganic acid and/or a precipitate of manganese dioxide should appear ; if neither a colouration nor a precipitate is produced, add a further 0·5 g. of sodium bismuthate and boil again for 5 minutes (1). Then add dropwise a concentrated solution of freshly prepared sulphurous acid or of sodium sulphite until the solution clears. Boil until all oxides of nitrogen are expelled (2). Cool the solution to about 15°C, add A.R. sodium bismuthate until no further appreciable alteration in colour ensues (about 0·25 g. $NaBiO_3$ for each 0·01 g. of Mn), add a further 0·5 g. excess, and stir the mixture for 2 to 3 minutes. Add 50 ml. of the prepared 3 per cent nitric acid, and filter through a Gooch (3) or sintered glass crucible into a 350 ml. conical flask. Wash the residue well with the 3 per cent nitric acid until free from permanganic acid ; this will generally require 50 to 100 ml., and the approximate volume should be noted. Run in slowly the ferrous ammonium sulphate solution from a burette until a slight excess is present (note the exact volume) as indicated by the disappearance of the permanganate colour (4). Titrate immediately with the 0·03N potassium permanganate to the first faint pink colouration (5). The addition of 3 ml. of syrupy phosphoric acid improves the end point.

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* Either Ridsdale's " Medium Carbon Steel, No. 2 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Carbon Steel ' E ' or ' R ' " (a British Chemical Standard) is suitable.

Standardise the ferrous ammonium solution by running a blank in the following manner. Into a 350 ml. Erlenmeyer flask place 50 ml. of 1 : 3 nitric acid, add a little sodium bismuthate, dilute with 50 to 100 ml. (use the volume of the wash liquid) of 3 per cent nitric acid, add an equal volume of the ferrous solution as was used in the determination, and titrate against the standard potassium permanganate solution. The difference between the titrations represents the permanganate equivalent of the permanganic acid formed in the determination.

Calculate the percentage of manganese in the sample of steel.

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}01099 \text{ g. Mn.}$$

Notes. 1. This preliminary oxidation with sodium bismuthate is to destroy any reducing substances, including carbonaceous matter, present which would subsequently slowly react with the permanganate.

2. All oxides of nitrogen must be removed, since these react with the permanganate. The reduction will also dissolve any manganese compounds that may have separated from the solution through the decomposition of the permanganic acid owing to the vigorous boiling.

3. The Gooch crucible containing asbestos must be freshly ignited before use.

4. The ferrous solution must be added as soon as the filtration and washing are complete, because the permanganic acid slowly decomposes.

5. This titration must be carried out immediately the ferrous solution has been added, because the ferrous solution reacts slowly with the nitric acid.

III, 61. Determination of formates and of formic acid.—*Discussion.* Potassium permanganate reacts slowly with formic acid in cold acid solutions ; in hot solutions, loss by volatilisation occurs. Formates in the presence of an alkali carbonate, *e.g.*, sodium or potassium carbonate, react quantitatively with potassium permanganate :

$$2KMnO_4 + 3H.COOK = KHCO_3 + 2K_2CO_3 + 2MnO_2 + H_2O.$$

This is one of the rare examples in which potassium permanganate has an equivalent weight of 1/3 of the formula weight or 1/3 mol :

$$MnO_4^- + 2H_2O + 3\epsilon = MnO_2 + 4OH^-,$$

or reacts in accordance with the hypothetical formula $K_2Mn_2O_8 = K_2O,2MnO_2, 3O$. In this method, the formic acid or formate is treated with an excess of sodium carbonate, and the standard potassium permanganate solution allowed to run into the hot formate solution until the clear liquid above the precipitate is just coloured pink. Some difficulty may be experienced in detecting the exact end point in the presence of the brown precipitate. The following procedure is therefore recommended. After the solution has acquired a distinct pink colour, it is strongly acidified with dilute sulphuric acid. a known excess of approximately $0{\cdot}1N$ sodium oxalate solution added, and the mixture warmed until the precipitate has dissolved. The excess of oxalate is then titrated with standard potassium permanganate solution.

In the modified procedure, the final end point is produced in acid solution. The final products of a chemical reaction are independent of the stages by which that reaction has been brought to completion, hence the permanganate reacts in accordance with the ionic equation :

$$MnO_4^- + 8H^+ + 5\epsilon = Mn^{++} + 4H_2O,$$

(or as $K_2O,2MnO,5O$) and its equivalent is 1/5 mol. The oxidation of the formic acid is essentially :

$$H.COOH + O = H_2O + CO_2,$$

hence 1 ml. N $KMnO_4 \equiv 0{\cdot}02301$ g. HCOOH.

The method is unreliable in the presence of much chloride.

For practice, the student may determine the purity of commercial sodium formate.

Procedure. Weigh out accurately about 1·7 g. of sodium formate and dissolve it in 500 ml. of water in a volumetric flask. Shake well. Transfer 25 ml. of this solution into a conical flask, add excess of sodium carbonate solution, followed by standard 0·1*N* potassium permanganate from a burette to the hot solution until the liquid has a distinct pink colour. Acidify strongly with dilute sulphuric acid, add 25 ml. of 0·1*N* sodium oxalate, and warm until the precipitate has dissolved and the permanganate colour has disappeared. Titrate the excess of oxalate against the standard permanganate solution. Titrate 25 ml. of the sodium oxalate solution with the permanganate solution ; the difference between this result and the total permanganate solution used gives the quantity of permanganate required to oxidise the formate. Repeat the determination with two other 25 ml. portions of the formate solution.

Calculate the percentage purity of the sample of sodium formate.

III, 62. Determination of selenium.—*Method A.* The selenious acid or selenite corresponding to about 0·1 g. of selenium is dissolved in 25 ml. of 40 per cent sulphuric acid, and diluted to 150 ml. Twelve grams of sodium phosphate (or phosphoric acid) is added (to prevent formation of manganese dioxide), followed by a considerable excess, at least 10 ml., of standard 0·1*N* potassium permanganate. After 30 minutes, the residual potassium permanganate is determined by the addition of a slight excess of 0·1*N* ferrous ammonium sulphate and back titration with standard 0·1*N* permanganate.

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}03948 \text{ g. Se.}$$

*Method B.** The reaction :

$$H_2SeO_3 + 4HI = Se + 2I_2 + 3H_2O$$

is quantitative if carbon disulphide is present to prevent the liberated iodine from being adsorbed on the selenium. 100 Ml. of an aqueous solution containing 0·05 to 0·10 g. of selenium as selenious acid are placed in a 250 ml. glass-stoppered bottle containing 10 ml. of 25 per cent hydrochloric acid and 20 ml. of carbon disulphide. Ten ml. of 10 per cent potassium iodide solution are added in a fine stream whilst the liquid is rotated. Shaking is continued for 1 minute, and the liberated iodine is then titrated with standard 0·1*N* sodium thiosulphate with shaking, starch being added as indicator.

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* This method should be given under Iodimetry and Iodometry, but is described here in order to have both methods for the determination of selenium together.

$$1 \text{ Ml. } N \ Na_2S_2O_3 \equiv 0{\cdot}01974 \text{ g. Se.}$$

Note. A mixture of selenious and tellurous oxides or acids can be estimated as follows. By the use of 0·1*N* potassium permanganate *both* oxides or acids are oxidised to the sexavalent condition. With 0·1*N* potassium dichromate, tellurium alone (see Section **III, 80,** *Method B*), is so oxidised. Hence by carrying out each oxidation on a different portion of the solution, each element can be determined.

It is not essential, however, to carry out titrations with two different samples, for if one portion is titrated with potassium dichromate solution, the tellurous tellurium will be oxidised ; the titration can then be completed with potassium permanganate solution. The pink colour appears sharply ; at the true end point the green colour of the chromic salt and the first drop of excess of permanganate solution gives a neutral grey tint. The effect is similar to that of " screened " methyl orange ; the colour change is green → grey → red.

OXIDATIONS WITH POTASSIUM DICHROMATE

III, 63. General discussion.—Potassium dichromate is not so powerful an oxidising agent as potassium permanganate (compare oxidation potentials in Table XVI, and also Fig. 1-17), but it has, however, several advantages over the latter substance. It can be obtained pure, is stable up to its fusion point and is therefore an excellent primary standard. Standard solutions of exactly known strength can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solution are stable indefinitely. Potassium dichromate is used only in acid solution, and is reduced rapidly at the ordinary temperature to a green chromic salt. It is not reduced by cold hydrochloric acid, provided the acid concentration does not exceed 1 or $2N$. Dichromate solutions are also less easily reduced by organic matter than are those of permanganate. Potassium dichromate is therefore of particular value in the determination of iron in iron ores : the ore is usually dissolved in hydrochloric acid, and the ferric iron reduced to the ferrous state with stannous chloride solution (see Section **III, 51A**) :

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

In acid solution, the reduction of potassium dichromate may be represented as :

$$Cr_2O_7^{--} + 14H^+ + 6\epsilon = 2Cr^{+++} + 7H_2O,$$

from which it follows (compare Section **I, 23**) that the equivalent weight is one sixth of the molecular weight, 294·21/6 or 49·035 g. A $0{\cdot}1N$ solution therefore contains 4·9035 g. per litre.*

With regard to the determination of the end point in titrations with potassium dichromate solutions three methods are available : ✓(i) with an external indicator, (ii) with an internal indicator, and (iii) potentiometrically. A general discussion of the principles underlying the potentiometric method has been given in Section **I, 51.**

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* For elementary students, the equivalent weight may be deduced from the hypothetical equations :

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O\,;$$

$$K_2Cr_2O_7 + 8HCl = 2KCl + 2CrCl_3 + 4H_2O + 3O.$$

From either of these equations, it follows that the equivalent weight is one sixth of the molecular weight ($K_2Cr_2O_7/6$).

The external indicator method was formerly widely used, but has become obsolete since the introduction of suitable oxidation-reduction indicators. It will only be described here for the sake of completeness, and also as an illustration of the use of an external indicator. Its widest application was in connexion with the titration of ferrous iron. A small crystal of pure potassium ferricyanide is repeatedly washed with distilled water in order to remove the superficial coating of the ferrocyanide. The washed crystal is dissolved in distilled water ($\ngtr$ 0·1 per cent solution) and drops of the solution, which should appear almost colourless or pale yellow, are placed on a white tile with the aid of a stirring rod. The acidified ferrous solution is titrated against the standard potassium dichromate solution. A drop of the ferrous solution is withdrawn from time to time with a thin glass rod and placed adjacent to a drop of the indicator ; the two drops are carefully allowed to coalesce.* At first a deep blue colour is produced where the drops mix, but as the addition of the dichromate solution is continued, this is replaced by a bluish green, then green shade, and the titration is completed when there is no trace of green and no change is apparent in the mixed drops. After the first titration, the dichromate solution is run in slowly into the diluted ferrous solution without testing to within 0·5 ml. of the previously determined end point, and then added a drop at a time, the liquid being tested after the addition of each drop.

The first internal indicator to be used for this titration was a 1 per cent solution of diphenylamine in concentrated sulphuric acid (J. Knop, 1924). Subsequently a 1 per cent solution of diphenylbenzidine in concentrated sulphuric acid and also a 0·2 to 0·3 per cent aqueous solution of sodium diphenylamine sulphonate were introduced. With these three indicators, phosphoric acid must be added ; the reason for this is that the phosphoric acid lowers the oxidation potential of the ferric-ferrous system by forming a complex with the ferric irons (for further details, see Section **I, 50**) These indicators impart a green colour to the ferrous solution, which deepens to a blue-green shortly before the end of the titration. At the end point an intense purple or blue-violet colouration is obtained, which remains permanent after shaking. The addition of phosphoric acid may be avoided by the use of *N*-phenylanthranilic acid or of tri-ortho-phenanthroline ferrous sulphate. The former is comparatively inexpensive, and is prepared by dissolving 1·07 g. of *N*-phenylanthranilic acid in 20 ml. of 5 per cent sodium carbonate solution and diluting to 1 litre; about 0·5 ml. is used in a titration. Tri-ortho-phenanthroline ferrous sulphate* is an expensive indicator, but since only one drop is necessary for each titration in a volume of 100 to 150 ml. owing to the intense colouration produced, the cost is in reality not high.† With both indicators it is best to work in a volume of approximately 300 ml. and the solution should be about 2*N* with respect to sulphuric acid; satisfactory results are also obtained when the solution is about 2*N* with respect to hydrochloric acid. If the dichromate solution is placed in the burette, the colour change at the end point is from orange to pale green for ferroin, and from green to violet red for *N*-phenylanthranilic acid. The reverse titration, dichromate with ferrous solution, is slower but definite, and the end point must be approached more slowly.

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* The above procedure may be replaced by the following which, although more time-consuming, has the advantage that the potassium ferricyanide solution is not exposed to the atmosphere of the laboratory for longer than is absolutely necessary. One drop of the indicator is set out on a white tile with a thin glass rod, the latter is washed and then employed to withdraw a drop of the titrated liquid, and the drops allowed to mix as described. The process is then repeated—the rod is washed, a drop of the ferricyanide solution placed on the tile, the rod washed again, a drop of the solution removed, etc., until the end point is reached.

It has already been mentioned that a standard solution of potassium dichromate can be prepared by weighing out accurately the requisite quantity of the pure dry salt and dissolving it in the appropriate quantity of water. Further standardisation is unnecessary. Sometimes, however, the problem of standardising a dichromate solution does arise. The best method is to use A.R. iron wire of 99·9 per cent purity (see Section **III, 46**). Ferrous ammonium sulphate may be employed in elementary work or in work requiring only moderate accuracy (see Section **III, 46**).

III, 64. Preparation of 0.1*N* potassium dichromate.—A.R. potassium dichromate has a purity of not less than 99·9 per cent.‡ Powder finely about 6 g. of the A.R. product in a glass or agate mortar, and heat for 30 to 60 minutes in an air oven at 140° to 150°C. Allow to cool in a desiccator. Weigh out accurately about 4·9 g. of the dry potassium dichromate into a weighing bottle and transfer the salt quantitatively to a 1 litre measuring flask (Section **II, 6A (iii)**, using a small funnel to avoid loss. Dissolve the salt in the flask in water and make up to the mark ; shake well. Alternatively, place a little over 4·9 g. of potassium dichromate in a weighing bottle, and weigh accurately. Empty the salt into a litre volumetric flask, and weigh the bottle again. Dissolve the salt in water, and make up to the mark. Mix thoroughly.

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* The abbreviation "ferroin" will be employed in all subsequent references to this indicator.

† A 4 oz. bottle of the prepared indicator, which is sufficient for about 2,000 titrations, costs about 10s. or 2$. This is a product of the G. F. Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio, U.S.A. It may also be purchased from the London agents, F. W. Berk and Co. Ltd., 52–54 Leadenhall Street, London, E.C.2, England.

‡ If a greater purity is required, or if only a pure grade of commercial salt is available, or if there is some doubt as to the purity of the salt, the following method of purification should be used. A concentrated solution of the salt

Calculate the exact normality by dividing the actual weight of the potassium dichromate employed by the theoretical weight for 1 litre of normal solution (49·035 g.). An exactly 0·1000*N* solution may be prepared by weighing out 4·904 g. of the salt and dissolving it in 1 litre of water in a measuring flask.

III, 65. Standardisation of potassium dichromate solution against iron.—For practice in this determination, use the 0·1*N* potassium dichromate prepared in the previous Section. Use the method described in Section **III, 48,** *Procedure C* with 0·2 g., accurately weighed, of A.R. iron wire. Alternatively, a flask fitted with a Bunsen valve (Fig. 3-6) may be employed : the air in the flask is similarly displaced by carbon dioxide. Titrate the cooled solution immediately against the dichromate solution, using either sodium diphenylamine sulphonate or *N*-phenylanthranilic acid as indicator. If the former is selected, add 6 to 8 drops of the indicator, followed by 5 ml. of syrupy phosphoric acid : titrate slowly with the dichromate solution, stirring well, until the pure green colour changes to a grey-green. Then add the dichromate solution dropwise until the first tinge of blue-violet, which remains permanent on shaking, appears. If the latter indicator is selected, add 200 ml. of 2*N* sulphuric acid, then 0·5 ml. of the indicator ; add the dichromate solution, with shaking until the colour changes from green to violet-red. Repeat the determination with two similar quantities of iron.

Calculate the normality of the potassium dichromate solution.

$$1 \text{ Ml. } N\ K_2Cr_2O_7 \equiv 0{\cdot}05584 \text{ g. Fe.}$$

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in hot water is prepared and filtered. The crystals which separate on cooling are filtered on a sintered glass filter funnel (Section **II, 12A**) and sucked dry. The resultant crystals are recrystallised again. The purified crystals are then dried at 180° to 200° C, ground to a fine powder in a glass or agate mortar, and again dried at 140° to 150°C to constant weight.

Note. For work requiring only moderate accuracy, A.R. ferrous ammonium sulphate may be used for standardisation. An approximately 0·1*N* solution is prepared by weighing out accurately about 9·8 g. of the solid and dissolving it in 250 ml. of 5 per cent sulphuric acid in a volumetric flask (**Section III, 48,** *Procedure D*). This is *slowly* titrated against the dichromate solution, using sodium diphenylamine sulphonate, *N*-phenylanthranilic acid or ferroin as indicator.

ANALYSES INVOLVING THE USE OF STANDARD POTASSIUM DICHROMATE SOLUTIONS.

III, 66. Determination of ferrous iron.—For practice in the titration, the student should determine the percentage of iron in crystallised ferrous sulphate $FeSO_4,7H_2O$, preferably of A.R. grade.

Weigh out accurately about 14 g. of ferrous sulphate crystals, dissolve in 450 ml. of 5 per cent sulphuric acid in a 500 ml. measuring flask, and make up to the mark with distilled water. Shake well. Titrate 25 ml. portions against the standard 0·1*N* potassium dichromate with sodium diphenylamine sulphonate (I)* and with *N*-phenylanthranilic acid (II) as examples of internal indicators, and with potassium ferricyanide as an external indicator.

Use 8 drops (say 0·4 ml.) of the indicator I, add 200 ml. of 2·5 per cent sulphuric acid, followed by 5 ml. of 85 per cent phosphoric acid, and titrate slowly and with constant stirring against the standard dichromate until the solution assumes a bluish-green or greyish-blue tint near the end point. Continue the titration, adding the dichromate solution dropwise and maintaining an interval of a few seconds between each drop, until the addition of one drop causes the formation of an intense purple or violet-blue colouration, which remains permanent after shaking and is unaffected on the further addition of the dichromate. Carry out 2 or at most 3 titrations; these should agree within 0·1 ml.

Use 0·5 ml. of indicator II. Add about 200 ml. of 2*N* sulphuric acid and then titrate against the 0·1*N* potassium dichromate until the colour changes from green to violet-red. This titration is sharp to within 1 drop. Carry out 2 or 3 further titrations, which should agree within 0·1 ml.

For the determination with the external indicator, use 25 ml. of the ferrous solution, add 100 ml. of *N* (*ca.* 2·5 per cent) sulphuric acid, and proceed as detailed in Section **III, 63.**

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* Or with diphenylamine or diphenylbenzidine; use 3 drops of the 1 per cent solution in concentrated sulphuric acid.

As in previous instances, carry out about three titrations; two successive values should agree within 0·1 ml.

Compare the mean volumes of the dichromate solution consumed in the three titrations with different indicators. These should not differ by more than 0·1 ml. Calculate the percentage of iron in the crystals.

$$1 \text{ Ml. } N\ K_2Cr_2O_7 \equiv 0{\cdot}05584 \text{ g. Fe.}$$

III, 67. Determination of ferric iron (iron in ferric ammonium sulphate).—Weigh out accurately about 12 g. of A.R. ferric alum $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, transfer to a 250 ml. volumetric flask, dissolve in water containing about 50 ml. of 2N (*ca.* 5 per cent) sulphuric acid, and make up to the mark with water. Shake well.

Of the various methods which can be employed for the reduction of the ferric iron, the stannous chloride method is very convenient, and, furthermore, illustrates the advantage of the use of dichromate solution when hydrochloric acid is present (compare Section **III, 46**).

Remove 25 ml. of the ferric solution, and reduce it with stannous chloride solution as described in Section **III, 51 A.** Then add 200 ml. of 2·5 per cent sulphuric acid, 5 ml. of syrupy phosphoric acid, and 0·3 to 0·4 ml. of sodium diphenylamine sulphonate indicator.* Titrate slowly and with constant stirring against standard 0·1*N* potassium dichromate to the first permanent violet-blue colouration. Carry out 2 further titrations; these should agree within 0·1 ml.

Calculate the percentage of iron in ferric alum.

III, 68. Determination of the total iron in an iron ore.—The iron ore of Section **III, 53** may be used, if desired. Weigh out accurately about 2 g. of the iron ore, dissolve it in dilute hydrochloric acid, and proceed exactly as described in Section **III, 53** to the point where a solution in a 250 ml. volumetric flask is obtained. Remove 50 ml. of this solution, heat to boiling, and reduce the ferric iron by the stannous chloride method (Section **III, 51 A**). Complete the estimation as detailed in the previous Section. Carry out three separate titrations, which should agree within 0·1 ml., and take the mean of the results.

Calculate the percentage of iron in the ore.

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* Alternatively 3 drops of diphenylamine or of diphenylbenzidine indicator may be used.

III, 69. Determination of ferrous and ferric iron in an iron ore.—For this estimation, spathic iron ore or any other suitable iron ore may be used. Determine first the total iron by the method described in the preceding Section.

Determine the ferrous iron as follows. Weigh out accurately about 0·4 g. of the finely-powdered iron ore into a 350 ml. flask fitted with wash-bottle tubes ; displace the air by carbon dioxide from a Kipp's apparatus or from a cylinder of the gas fitted with a reducing valve. Open the flask momentarily and pour in 30 ml. of 1 : 1-hydrochloric acid. Replace the rubber stopper and tubes, and warm in a slow stream of carbon dioxide until the ore has been completely attacked and no further solution takes place. A whitish residue of silica remains in most cases. Cool in a stream of carbon dioxide, wash down the tubes and the neck of the vessel with a little cold, air-free distilled water, dilute with 200 ml. of 2·5 per cent sulphuric acid (which has been prepared with air-free water), add 5 ml. of syrupy phosphoric acid and 0·3 to 0·4 ml. of sodium diphenylamine sulphonate indicator, and titrate slowly and with constant stirring against standard 0·1*N* potassium dichromate to the first permanent violet-blue colouration. Alternatively, 1 or 2 drops of ferroin may be used as indicator ; here the addition of phosphoric acid is superfluous. Repeat the determination with two other similar quantities of the ore.

Calculate the percentages of total iron and ferrous iron in the ore. The difference between these two values gives the percentage of iron present in the ferric state.

III, 70. Determination of chromium in a chromic salt.—*Discussion.* Chromic salts are oxidised to dichromates by boiling with excess of a persulphate solution in the presence of a little silver nitrate (catalyst). The excess of persulphate remaining after the oxidation is complete is destroyed by boiling the solution for a short time. The dichromate content of the resultant solution is determined by the addition of excess of a standard ferrous solution and titration of the excess of the latter with standard 0·1*N* potassium dichromate.

For practice in this determination, the student may determine the percentage of chromium in A.R. chrome alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$.

Procedure. Weigh out accurately about 2·5 g. of chrome alum, and dissolve it in 50 ml. of distilled water. Add 20 ml. of *ca.* 0·1*N* silver nitrate solution, followed by 50 ml. of a 10 per cent solution of ammonium or potassium persulphate. Boil the liquid gently (using a Fisher " speedyvap " beaker cover) for 20 minutes. Cool, and dilute to 250 ml. in a volumetric flask. Remove 50 ml. of the solution with a pipette, add 50 ml. of 0·1*N* ferrous ammonium sulphate solution (Section **III, 48,** *Procedure D*), 200 ml. of 2*N* sulphuric acid and 0·5 ml. of *N*-phenylanthranilic acid indicator. Titrate the excess of the ferrous salt with standard 0·1*N* potassium dichromate until the colour changes from green to violet-red.

Standardise the ferrous ammonium sulphate solution against the 0·1*N* potassium dichromate using *N*-phenylanthranilic acid as indicator (Section **III, 66**). Calculate the volume of the ferrous solution which was oxidised by the dichromate originating from the chrome alum, and from this the percentage of chromium in the sample.

$$1 \text{ Ml. } N \text{ Fe}^{++} \equiv 0{\cdot}01734 \text{ g. Cr.}$$

III, 71. Determination of chromium in chromite.—*Discussion.* The highly refractory mineral chromite is brought into solution by fusion with excess of sodium peroxide :

$$2FeCr_2O_4 + 7Na_2O_2 = 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O.$$

Upon leaching the melt with water, the sodium chromate dissolves and the iron is precipitated as ferric hydroxide :

$$NaFeO_2 + 2H_2O = NaOH + Fe(OH)_3 ;$$
$$2Na_2O + 4H_2O = 4NaOH.$$

The excess of peroxide is decomposed by boiling the alkaline solution. The precipitate is filtered off after diluting the solution ; the filtrate is acidified with hydrochloric acid, a known volume of excess of ferrous ammonium sulphate solution is added, and the excess of ferrous salt is titrated with standard potassium dichromate solution.

$$2Na_2CrO_4 + 2HCl = Na_2Cr_2O_7 + 2NaCl + H_2O ;$$
$$Na_2Cr_2O_7 + 6FeSO_4 + 14HCl$$
$$= 2CrCl_3 + 2NaCl + 2Fe_2(SO_4)_3 + 2FeCl_3 + 7H_2O.$$

Procedure. Weigh out accurately about 0·5 g. of the very finely powdered ore* into a 30 to 35 ml. nickel, or heavy-walled porcelain, crucible, add 4 g. of sodium peroxide, and mix thoroughly by means of a thin glass rod. Remove any powder adhering to the rod by stirring about 1 g. of sodium peroxide with it ; cover the mixture in the crucible with this peroxide. Place the lid on the crucible, and gently heat the covered crucible in the fume cupboard over a small flame until the mass is quite liquid (about 10 minutes) ; keep fused for a further 10 minutes at a dull red heat. Allow to cool, and when a solid crust has formed, add 4 g. more of the sodium peroxide, and fuse the mixture again at a cherry-red heat for 10 minutes. Allow the crucible to cool and place it in a 600 ml. Pyrex or Hysil beaker containing a little distilled water. Cover the beaker with a clock glass (or with a Fisher " speedyvap " beaker cover), add a little warm water, and, after the violent action has subsided, remove the crucible and wash it thoroughly, collecting the washings in the same beaker. Boil the liquid for 30 minutes, keeping the beaker covered (this decomposes the hydrogen peroxide), add 250 ml. of boiling water, and allow the precipitate to settle. Filter through a hardened 15 cm. filter paper or, better, through a sintered glass crucible,* and wash the residue thoroughly with boiling water until free from chromate. (The residue should be completely soluble in concentrated hydrochloric acid ; no black gritty particles should remain. If this is not the case, decomposition is not complete, and the determination must be started afresh.) Evaporate the filtrate to about 200 ml., cool, and add 9*N* sulphuric acid cautiously until acid. Cool, and transfer to a 250 ml. measuring flask, and make up to the mark with distilled water. Shake well. Remove 50 ml. of this solution with a pipette, add 50 ml. of 0·1*N* ferrous ammonium sulphate (Section **III, 48,** *Procedure D*); 200 ml. of 2*N* sulphuric acid, and 0·5 ml. of *N*-phenylanthranilic acid indicator. Titrate with standard 0·1*N* potassium dichromate until the colour changes from green to violet-red. Alternatively, take 50 ml. of the solution, add 50 ml. of 0·1*N* ferrous ammonium sulphate, 5 ml. of syrupy phosphoric acid and 0·4 ml. of sodium diphenylamine sulphonate indicator ; dilute to 200 ml., and titrate with standard 0·1*N* potassium dichromate until the green colour changes to violet-blue. Repeat until two titrations agree within 0·1 ml.

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* Ridsdale's " Chrome Iron Ore, No. 27 " (one of the Analysed Samples for Students) is suitable for this determination.

The ferrous ammonium sulphate solution must be standardised by titration against the 0·1*N* potassium dichromate ; the same indicator as was employed in the above determination must be used.

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* If the latter is used, it is unnecessary to add more than 150 ml. of boiling water ; the subsequent concentration is then avoided.

Calculate the volume of the ferrous solution which was oxidised by the dichromate originating from the chromite, and from this the percentage of chromium in the original ore.

$$1 \text{ Ml. } N \text{ Fe}^{++} \equiv 1 \text{ ml. } N \text{ K}_2\text{Cr}_2\text{O}_7 \equiv 0{\cdot}02534 \text{ g. Cr}_2\text{O}_3 \equiv 0{\cdot}01734 \text{ g. Cr.}$$

III, 72. Determination of manganese in steel or in manganese ore (Pattinson's method).—*Discussion.* When a solution containing iron, zinc and manganese salts is treated with bromine water and calcium carbonate, all the manganese is precipitated in the quadrivalent condition as the manganite (*e.g.*, ZnO,MnO_2). The precipitate is dissolved in excess of ferrous solution, and the excess of the latter titrated with standard potassium dichromate solution.

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$$

Procedure. Weigh out 2·5 g. of the steel or 1 g. of the manganese ore* and dissolve it in 50 ml. of concentrated hydrochloric acid in a covered beaker. Oxidise with a little nitric acid and evaporate to a small volume in order to expel the excess of acid. Transfer to a 250 ml. measuring flask, after filtering through a sintered glass crucible, if necessary. Make up to the mark with distilled water, and shake thoroughly. Transfer 50 ml. of the solution into a litre beaker, add 30 ml. of 3 per cent zinc chloride solution, and then add pure calcium carbonate in small quantities at a time until the liquid is almost neutralised, but still remains clear. Add 100 ml. of *saturated* bromine water, and then more calcium carbonate with constant stirring until an excess of about 1 gram remains undissolved. Add 700 ml. of boiling water to the contents of the beaker, stir well, and allow the insoluble residue to settle for a few minutes. If the supernatant liquid is violet, due to permanganic acid, add 1 to 2 drops of alcohol, boil until colourless, and again allow the precipitate to settle. Decant the liquid through a funnel containing a large hardened filter paper ; it is better to allow the latter to rest on a Whatman filter cone (hardened, No. 51), so that suction may be applied. Wash the precipitate 4 times by decantation, using 300 ml. of hot water each time. Transfer the precipitate to the filter, rinsing out the beaker well without making any attempt to remove the precipitate which adheres to the glass. Wash the precipitate with hot water until the filtrate no longer turns starch-potassium iodide paper blue. Place the filter paper and precipitate in the original beaker, add 50 ml. of freshly standardised 0·1*N* ferrous ammonium sulphate and 50 ml. of 9*N* sulphuric acid. Stir the mixture until the precipitate has entirely dissolved. Titrate the excess of ferrous salt with standard 0·1*N* potassium dichromate. Repeat the estimation with two other 50 ml. portions of the solution.

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* Suitable samples are Ridsdale's " Steel, Nos. 1, 2, 3, or 21 " and " Pyrolusite (Mn) Ore, No. 21 " (Analysed Samples for Students) or the Bureau of Analysed Samples " Carbon Steels, ' E ' or ' R ' " and " Mang. Ore ' A ' " (British Chemical Standards).

Calculate the percentage of manganese in the sample.

$$1 \text{ Ml. } N\ K_2Cr_2O_7 \equiv 0{\cdot}02747 \text{ g. Mn.}$$

OXIDATIONS WITH CERIC SULPHATE

III, 73. General discussion.—As a result of the systematic investigations, commenced in 1928, of Willard and Young, of Furman and his co-workers, and of Atanasiu, the use of ceric sulphate as a volumetric oxidising agent has become firmly established. Ceric sulphate is a powerful oxidation agent; its oxidation potential in 1 to 8*N* sulphuric acid at 25°C is 1·43 ± 0·1 volts (compare Section **I, 46**). It can be used only in acid solution, best in 0·5*N* or higher concentrations: in neutral or alkaline solutions, basic ceric or perceric salts respectively may be formed. The solution has an intense yellow colour, and in hot solutions which are not too dilute, the end point may be detected without an indicator; the latter procedure, however, necessitates the application of a blank correction, and it is therefore preferable to add a suitable indicator. It should be noted, however, that the self-colour of ceric solutions is less pronounced than that of permanganate solutions, and the titration with an oxalate cannot be so readily carried out (compare Section **III, 76**).

The advantages of ceric sulphate as a standard oxidising agent are:

1. Ceric sulphate solutions are remarkably stable over prolonged periods. They need not be protected from light, and may even be boiled for a short time without appreciable change in concentration. The stability of sulphuric acid solutions coveres the wide range of 10 to 40 ml. of concentrated sulphuric acid per litre. It is evident, therefore, that an acid solution of ceric sulphate surpasses a permanganate solution in stability.

2. Ceric sulphate may be employed in the determination of reducing agents in the presence of a high concentration of hydrochloric acid (contrast potassium permanganate, Section **III, 46**).

3. Ceric solutions in 0·1*N* solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other volumetric apparatus.

4. It was formerly generally assumed that the reaction involved the simple valency change:

$$Ce^{++++} + \epsilon \rightleftharpoons Ce^{+++};$$

the equivalent weight of a ceric salt is therefore the molecular weight. With permanganate, of course, a number of reduction products are possible according to the experimental conditions.

Recent work of G. F. Smith and Getz (1938) upon the single electrode potentials of the ceric, cerous system in the presence of varying concentrations of sulphuric, nitric and perchloric acids has yielded the following results :

Acid Concentration	*Single Electrode Potential Values (Volts)*		
N	H_2SO_4	HNO_3	$HClO_4$
1	1·44	1·61	1·70
2	1·44	1·62	1·71
4	1·43	1·61	1·75
6	—	—	1·82
8	1·42	1·56	1·87

Since the single electrode potential varies considerably with the anion of the acid used but only slightly with its concentration, these authors conclude that the results support the view that the following equilibria are present in the three solutions respectively :

$$\frac{[\mathrm{Ce(SO_4)_3}^{--}]}{[\mathrm{Ce}^{++++}] \times [\mathrm{SO_4}^{--}]^3}\,; \qquad \frac{[\mathrm{Ce(NO_3)_6}^{--}]}{[\mathrm{Ce}^{++++}] \times [\mathrm{NO_3}^{-}]^6}\,;$$
$$\frac{[\mathrm{Ce(ClO_4)_6}^{--}]}{[\mathrm{Ce}^{++++}] \times [\mathrm{ClO_4}^{-}]^6}\,.$$

No measurements are at present available of the instability constants of the various ions (Section **I, 12**), but it would appear that the ionic equilibria present, say, with ceric sulphate in sulphuric acid solution could be represented by :

$$\mathrm{H_2[Ce(SO_4)_3]} \rightleftharpoons 2\mathrm{H}^+ + [\mathrm{Ce(SO_4)_3}]^{--} \rightleftharpoons 2\mathrm{H}^+ + \mathrm{Ce}^{++++} + 3\mathrm{SO_4}^{--},$$

so that the actual reaction which takes place in the presence of a reducing agent, particularly for ceric sulphate in sulphuric acid solution which has been most extensively studied, is indeed :

$$\mathrm{Ce}^{++++} + \epsilon \rightleftharpoons \mathrm{Ce}^{+++}.$$

5. The cerous ion is colourless (compare colourless manganous ion from potassium permanganate, and green chromic ion from potassium dichromate).

6. Ceric sulphate is a very versatile oxidising agent. It may be employed in most titrations in which permanganate has been used and also for other estimations.

7. The indicators which have been used in ceric sulphate titrations include : diphenylamine, diphenylbenzidine, sodium diphenylamine sulphonate, methyl red (with these four indicators, phosphoric acid must be present), erio glaucine, erio green, xylene cyanol FF, ferroin, and *N*-phenylanthranilic acid. The last three indicators give the most striking colour changes, and thus render the determination of the correct end point a very easy matter : moreover, the addition of phosphoric acid is unnecessary.

8. Ceric sulphate solutions can be readily standardised against *inter alia* arsenious oxide, pure iron, and ferrous solutions, and also indirectly against sodium oxalate (Section **III, 76**).

For some years it was customary to prepare ceric sulphate solutions from commercial ceric oxide or cerous oxalate. This somewhat tedious process was doubtless responsible for the limited application of ceric sulphate as a volumetric oxidising agent. Pure ceric sulphate and also the more soluble ceric ammonium sulphate (composition approximately $Ce(SO_4)_2,2(NH_4)_2SO_4,2H_2O$) is now marketed at a very moderate price.* The latter is indeed the cheapest ceric salt, suitable for volumetric work, at present available on the market ; it suffers, however, from the disadvantage that it is a hydrated salt. With the discovery by G. F. Smith, Sullivan and Frank in 1936 of a method for preparing pure ammonium hexanitrato-cerate $(NH_4)_2[Ce(NO_3)_6]$, ceric oxidimetry has reached the stage when it should be available and used in every laboratory. Two crystallisations of the inexpensive and readily obtainable commercial " ceric ammonium nitrate " from concentrated nitric acid in the presence of ammonium nitrate give a product of at least 99·5 per cent purity ; with one crystallisation the purity exceeds 99 per cent, and this substance is sufficiently pure for most purposes. The above authors propose the substance as a primary standard, but in view of the ease with which ceric sulphate solutions may be standardised against arsenious oxide, etc., the writer prefers to avoid the somewhat lengthy process of drying the recrystallised ceric ammonium nitrate in a desiccator over potassium hydroxide in order to remove the last traces of nitric acid. He converts a known weight of ceric ammonium nitrate into ceric sulphate by evaporating with concentrated sulphuric acid, dissolves the resultant ceric sulphate in dilute sulphuric acid, and then standardises the solution.† One litre of 0·1*N* ceric sulphate, prepared from recrystallised ceric ammonium nitrate, costs about 1s. (or about 20 cents).

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* Marketed by the G. F. Smith Chemical Co., Columbus, Ohio, U.S.A. ; the English agents are F. W. Berk and Co. Ltd., 52–54 Leadenhall Street, London, E.C.3. Also by Johnson, Matthey and Co. Ltd., Hatton Garden, London, E.C.1.

† Unpublished work in the author's laboratory by S. J. Hart and A. S. Nickelson (1937) has shown that ceric ammonium nitrate may be dissolved directly in 2*N* sulphuric acid, and employed for many purposes in which ceric sulphate is used. However, for some determinations the presence of nitrate ions may be harmful, and, since the conversion into ceric sulphate is so simple a process, it is best, as a general rule, to work with solutions of ceric sulphate.

III, 74. Preparation of 0·1*N* ceric sulphate.—*Method A*. Dissolve 100 grams of commercial ceric ammonium nitrate in 270 ml. of boiling hot concentrated nitric acid, and then dissolve 30 g. of ammonium nitrate in the solution. Filter the boiling hot solution through a large Jena sintered glass funnel (Section **II, 12A**), and cool the filtrate in ice or, preferably, allow it to stand overnight in a covered beaker. Filter off the separated solid on a similar sintered glass funnel, and leave it on the pump for 1 to 2 hours in order to remove the excess of nitric acid. The yield is 90 per cent. Crystallise the recrystallised ceric ammonium nitrate once more if a product of very high purity is required ; for most purposes, as already pointed out, a second recrystallisation is unnecessary. Dry the recrystallised solid at 110°C for 1·5 hours. The most convenient method is to spread the solid in thin layers on clock glasses, and to heat the latter either in a Jena glass air bath (Fig. 2-13) or in the asbestos-lined air bath described in Section **II, 13F**. (If perfectly pure ceric ammonium nitrate is required, the twice recrystallised product must be further dried in a vacuum desiccator (Fig. 2-10, *B*) over potassium hydroxide to constant weight.) For routine work, evaporate 55 g. of the dried ceric ammonium nitrate (equivalent and molecular weight = 548·27) almost to dryness with excess (48 ml.) of concentrated sulphuric acid either in a Pyrex evaporating dish or in a shallow (" Bako ") beaker. Dissolve the resultant ceric sulphate in *N* sulphuric acid (28 ml. of concentrated sulphuric acid to 1 litre of water), transfer quantitatively to a 1 litre volumetric flask, add *N* sulphuric acid until near the graduation mark, and then make up to the mark with distilled water. Shake thoroughly.

Method B. The molecular and also the equivalent weights of ceric sulphate $Ce(SO_4)_2$ and ceric ammonium sulphate $Ce(SO_4)_2,2(NH_4)_2SO_4,2H_2O$ are 332·25 and 632·57 respectively. Dissolve 65 to 70 g. of ceric ammonium sulphate in a solution prepared by adding 28 ml. of concentrated sulphuric acid to 500 ml. of water ; the mixture is stirred until dissolved. Transfer to a 1 litre measuring flask and make up to the mark with distilled water. Shake well.

Alternatively, weigh out 40 g. of anhydrous ceric sulphate into a 600 ml. beaker, add 56 ml. of 1 : 1-sulphuric acid, and stir, with frequent additions of water and gentle warming, until the salt is dissolved. Transfer to a 1 litre volumetric flask, and, when cold, dilute to the mark. Shake thoroughly.

Note. These salts need not be of a high grade of purity. The presence of other rare earths introduces no complications, since these metals do not exhibit any variations in valency. If the salts are impure, it will of course be necessary to increase the quantities given above by 10 to 75 per cent according to the percentage of cerium present.

III, 75. Standardisation of ceric sulphate solutions.—*Discussion.* The most trustworthy method for standardising ceric sulphate solutions is with pure arsenious oxide. The reaction between ceric sulphate and arsenious acid is very slow at the ordinary temperature ; it is necessary to add a trace of osmium tetroxide or, less satisfactorily, iodine chloride as a catalyst. The arsenious oxide is dissolved in sodium hydroxide solution, the solution acidified with dilute sulphuric acid, 2 drops of "osmic acid" added, followed by the indicator, and the resultant solution is titrated against the ceric sulphate solution to the first sharp colour change. As already pointed out (Section **III, 73**) the most satisfactory indicators are : (i) a 0·1 per cent solution of xylene cyanol FF (0·5 ml.)* ; (ii) 0·025*M* ferroin† (1 or 2 drops) ; and (iii) 0·005*M* *N*-phenylanthranilic acid‡ (0·5 ml.). The colour changes are respectively : (i) yellowish-green to orange ; (ii) orange-red to very pale blue ; and (iii) yellowish-green to purple.

$$As_2O_3 + 6NaOH = 2Na_3AsO_3 + 3H_2O.$$

$$2Na_3AsO_3 + 3H_2SO_4 = 2H_3AsO_3 + 3Na_2SO_4.$$

$$H_3AsO_3 + 2Ce(SO_4)_2 + H_2O = H_3AsO_4 + Ce_2(SO_4)_3 + H_2SO_4.$$

Another method is to use pure iron. A known weight is dissolved in dilute sulphuric acid, and the resultant ferrous solution titrated with the ceric sulphate solution ; any of the three indicators, mentioned above, may be employed.

$$2FeSO_4 + 2Ce(SO_4)_2 = Fe_2(SO_4)_3 + Ce_2(SO_4)_3.$$

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* The end point is difficult to detect by artificial light with this indicator.

† This indicator solution may be purchased (see footnote in Section **III, 63**) or may be prepared, if desired, as follows. Dissolve 1·485 g. of ortho-phenanthroline monohydrate $C_{12}H_8N_2,H_2O$ (molecular weight, 198 ; melting point, 90° to 100°C) in 100 ml. of 0·025*M* ferrous sulphate, prepared by dissolving 0·695 g. of crystallised ferrous sulphate $FeSO_4,7H_2O$ in 100 ml. of water.

‡ Dissolve 1·07 g. of *N*-phenylanthranilic acid in 20 ml. of 5 per cent sodium carbonate solution, and dilute to 1 litre.

For work not requiring a very high degree of accuracy, pure ferrous ammonium sulphate may be used (see remarks in Section **III, 46**).

Solutions of ceric sulphate may be standardised against sodium oxalate in hot dilute sulphuric acid solution. Here no satisfactory indicator is available at present, because the known oxidation-reduction indicators are oxidised before the equivalent point is reached. Contrary to the experience of other workers, the writer could not obtain satisfactory results by the use of iodine chloride as catalyst and ferroin as indicator. The end point may, however, be determined potentiometrically, or by the addition of ceric sulphate solution to the hot solution of oxalate to the first appearance of a pale yellow colour. There is an appreciable blank correction in the latter procedure, and the method is not recommended except for approximate work.

Procedure A. **Standardisation with arsenious oxide.** Weigh out accurately about 0·25 g. of A.R. arsenious oxide, previously dried at 105° to 110°C for 1 to 2 hours, and transfer to a 400 ml. beaker or to a 350 ml. conical flask. Add 20 ml. of 5 per cent sodium hydroxide solution, and warm the mixture gently until the arsenious oxide has *completely* dissolved (1). Cool to room temperature, and add 100 ml. of water, followed by 25 ml. of 1 : 5 sulphuric acid. Then add 3 drops of 0·01*M* osmium tetroxide solution (0·25 g. of osmium tetroxide dissolved in 100 ml. of 0·1*N* sulphuric acid) and 0·5 ml. of *N*-phenylanthranilic acid indicator (or 0·5 ml. of xylene cyanol FF, or 1 to 2 drops of ferroin). Titrate with the 0·1*N* ceric sulphate solution until the first sharp colour change occurs (see *Discussion* above). Repeat with two other samples of approximately equal weight of arsenious oxide.

Calculate the normality of the ceric sulphate solution (for details, see Section **III, 48,** *Procedure A*).

Note. 1. Elementary students may prepare 250 ml. of an approximately 0·1*N* arsenious oxide solution, and titrate 25 ml. of this against the ceric solution as described above. Full details for the preparation of the solution and the method for the calculation of the result will be found in Section **III, 48,** *Procedure A*, Note 1.

Procedure B. **Standardisation against pure iron.** Weigh out accurately 0·15 to 0·20 g. of A.R. iron wire, and then proceed exactly as described in Section **III, 48,** *Procedure C*. Titrate the resultant ferrous solution against the ceric sulphate solution, using any of the indicators referred to in the Discussion.

Another method, which incidentally utilises the stannous chloride process of reduction, is the following. Weigh out accurately about 0·20 g. of A.R. iron wire into a 400 ml. beaker or into a 350 ml. conical flask. Add 5 ml. of water and 10 ml. of concentrated hydrochloric acid. Warm the solution until all the iron has dissolved. Heat the solution to boiling, and add freshly prepared 0·5*N* stannous chloride, dropwise and with constant stirring, from a burette or separating funnel (Section **III, 51A**) until the hot solution no longer shows any yellow colour and a few drops of the reducing agent causes the colour to change from yellow to very pale green. Cool, add 5 ml. of concentrated hydrochloric acid, dilute the solution with cold air-free water to 250 ml., and add 10 ml. of a saturated solution of mercuric chloride. A slight white silky precipitate of mercurous chloride should be formed, sometimes after 1 to 2 minutes. (If the precipitate is bulky or grey in colour, the solution should be rejected, and the estimation repeated.) Add a drop or two of ferroin and titrate slowly with the ceric sulphate solution until the sharp colour change from red to a faint yellow or green colour occurs. Alternatively, add 5 ml. of syrupy phosphoric acid, 0·5 ml. of sodium diphenylamine sulphonate, then titrate the mixture against the ceric sulphate solution (proceed slowly near the end point) until the solution assumes a distinct purple tint. Repeat with two other samples of the A.R. iron wire.

Calculate the normality of the ceric sulphate solution.

Procedure C. **Standardisation against ferrous ammonium sulphate.** As pointed out in Section **III, 46,** this method is only suitable for work requiring moderate accuracy or for elementary students. Prepare an approximate 0·1*N* solution of ferrous ammonium sulphate (Section **III, 48**, *Procedure D*). Transfer 25 ml. of this solution to a conical flask, add 25 ml. of *N*-sulphuric acid, and the appropriate quantity of xylene cyanol FF, ferroin or *N*-phenylanthranilic acid (see Discussion above) ; titrate with the ceric sulphate solution to the first sharp colour change. Carry out 2 or at most 3 titrations ; these should agree within 0·1 ml.

Alternatively, the ferrous solution may be placed in the burette, and 25 ml. portions of the ceric solution titrated. The end points are equally satisfactory, although when once the colour of the ceric solution has been bleached, it is advisable to add the ferrous solution slowly.

Calculate the normality of the ceric sulphate solution.

ANALYSES INVOLVING THE USE OF STANDARD CERIC SULPHATE SOLUTIONS

Practically all the determinations described under potassium permanganate and potassium dichromate may be carried out with ceric sulphate. Use is made of the various indicators already detailed and also, in some cases where great accuracy is not required, of the pale yellow colour produced by the ceric sulphate itself. Only a few determinations will therefore be considered in some detail.

III, 76. Determination of oxalates ($H_2C_2O_4$ in crystallised oxalic acid).—*Discussion.* This determination will give the student practice in the titration of oxalates with ceric sulphate solution. Two methods may be used. In the first, the ceric sulphate solution is run into the hot solution of oxalic acid acidified with dilute sulphuric acid until the solution acquires a pale yellow colour, the ceric solution thus acting as its own indicator.

$$H_2C_2O_4 + 2Ce(SO_4)_2 = 2CO_2 + Ce_2(SO_4)_3 + H_2SO_4.$$

In the second procedure, a known excess of the ceric solution is added to the oxalic acid solution, the mixture warmed for 5 minutes at 50°C in order to complete the reaction, and, after cooling, the excess of ceric sulphate is titrated with ferrous ammonium sulphate solution, using *N*-phenylanthranilic acid or ferroin as indicator.

The latter method provides an excellent means for *standardising* ceric sulphate solutions. Thus if roughly equivalent solutions (say, of about 0·1*N* strength) of ceric sulphate and of ferrous ammonium sulphate be titrated, the relative concentrations will be found. Now if a known weight of A.R. sodium oxalate be dissolved in dilute sulphuric acid, excess of the ceric sulphate solution added, the mixture heated at 50°C for 5 minutes, and, after cooling, back titrated with the ferrous ammonium sulphate solution, then the volume of ceric sulphate solution equivalent to the known weight of the pure sodium oxalate is obtained. The normality of the ceric sulphate solution can then be readily calculated.

Procedure. Weigh out accurately about 3·15 g. of A.R. crystallised oxalic acid ($H_2C_2O_4,2H_2O$), dissolve it in water, and make up to 500 ml. in a volumetric flask. Shake well. Transfer 25 ml. of this solution with a pipette into a conical flask, add 25 ml. of *N* sulphuric acid, heat to 70° to 80°C, and titrate against the 0·1*N* ceric sulphate until the solution assumes a faint yellow colour. Repeat the titration with 50 ml. of *N* sulphuric acid, heat to 70° to 80° C, and add the ceric sulphate solution until the solution has the same colour as in the previous titration. Subtract this blank correction from the volume of 0·1*N* ceric sulphate consumed in the titration with the oxalic acid solution. Carry out two other titrations with the oxalic acid solution ; the values should agree within 0·1 to 0·2 ml.

Calculate the percentage of $H_2C_2O_4$ in the oxalic acid crystals.

$$1 \text{ Ml. } N \text{ Ce(SO}_4)_2 \equiv 0{\cdot}04502 \text{ g. } H_2C_2O_4.$$

For the alternative method, prepare an approximately 0·1*N* solution of ferrous ammonium sulphate (Section **III, 48,** *Procedure D*). Place this in the burette and titrate it against a mixture of 25 ml. of the 0·1*N* ceric sulphate and 25 ml. of *N* sulphuric acid, using ferroin (1 drop) or *N*-phenylanthranilic acid (0·5 ml.) as indicator. Measure out 25 ml. of the oxalic acid solution into a conical flask, add 50 ml. of 0·1*N* ceric sulphate and 50 ml. of *N* sulphuric acid. Warm the mixture at 50°C for 5 minutes, cool, and titrate the excess of ceric sulphate with the ferrous solution, employing the same indicator as in the first titration. Repeat the determination with two other 25 ml. portions of the oxalic acid solution ; the titrations should agree within 0·1 ml.

Calculate the volume of the 0·1*N* ceric sulphate that has reacted with the oxalic acid, and thence the percentage of $H_2C_2O_4$ in the oxalic acid crystals.

III, 77. Determination of iron in an iron ore.—The procedure is identical with that given in Section **III, 68,** except that after the reduction with stannous chloride, addition of excess of mercuric chloride solution and 200 ml. of 2·5 per cent sulphuric acid, 1 or 2 drops of ferroin or 0·5 ml. of *N*-phenylanthranilic acid is added. The mixture is then titrated with 0·1*N* ceric sulphate to the first sharp colour change.

Calculate the percentage of iron in the ore.

$$1 \text{ Ml. } N \text{ Ce(SO}_4)_2 \equiv 0{\cdot}05584 \text{ g. Fe.}$$

III, 78. Determination of ferrocyanides ($K_4[Fe(CN)_6]$ in crystallised potassium ferrocyanide).—For practice in this estimation, use A.R. potassium ferrocyanide $K_4[Fe(CN)_6],3H_2O$; commercial potassium ferrocyanide will, however, serve equally well. Weigh out accurately about 1 g. of the potassium ferrocyanide, and dissolve it in 100 ml. of distilled water in a conical flask. Add 25 ml. of 1 : 5 sulphuric acid or 25 ml. of 1 : 1 hydrochloric acid, and 1 drop of ferroin or 0·5 ml. of *N*-phenylanthranilic acid. Titrate with standard 0·1*N* ceric sulphate to the first sharp colour change. Repeat the determination with two other samples of the potassium ferrocyanide.

$$2K_4[Fe(CN)_6] + 2Ce(SO_4)_2 = 2K_3[Fe(CN)_6] + Ce_2(SO_4)_3 + K_2SO_4.$$

Calculate the percentage of $K_4[Fe(CN)_6]$ in the crystals.

$$1 \text{ Ml. } N\ Ce(SO_4)_2 \equiv 0{\cdot}3684 \text{ g. } K_4[Fe(CN)_6].$$

III, 79. Determination of nitrites.—*Discussion.* Satisfactory results are obtained by adding the nitrite solution to excess of standard 0·1*N* ceric sulphate, and determining the excess of ceric sulphate with a standard ferrous solution (compare Section **III, 58**).

$$2Ce^{++++} + NO_2^- + H_2O = 2Ce^{+++} + NO_3^- + 2H^+.$$

For practice, the student may determine the percentage of NO_2 in potassium nitrite, or the purity of sodium nitrite, preferably of A.R. quality.

Procedure. Weigh out accurately about 1·5 g. of sodium nitrite and dissolve it in 500 ml. of boiled-out water in a volumetric flask. Shake thoroughly. Place 50 ml. of standard 0·1*N* ceric sulphate in a conical flask, and add 10 ml. of 4*N* sulphuric acid. Transfer 25 ml. of the nitrite solution to this flask by means of a pipette, and keep the tip of the pipette below the surface of the liquid during the addition. Allow to stand for 5 minutes, and titrate the excess of ceric sulphate against standard 0·1*N* ferrous ammonium sulphate, using ferroin or *N*-phenylanthranilic acid as indicator. Repeat the titration with two further portions of the nitrite solution. Standardise the ferrous solution by titrating it with 25 ml. of the ceric solution in the presence of dilute sulphuric acid (Section **III, 75C**).

Determine the volume of the standard ceric sulphate solution which has reacted with the nitrite solution, and therefrom calculate the purity of the sodium nitrite employed.

$$1 \text{ Ml. } N\ Ce(SO_4)_2 \equiv 0{\cdot}02301 \text{ g. } NO_2.$$

III, 80. Determination of tellurium. *Method A.* A measured excess of standard 0·1N ceric sulphate is added to the tellurous solution (200 ml.) containing 10 ml. of concentrated hydrochloric acid and about 0·05 g. of chromium sulphate as catalyst.* The solution is boiled for 10 minutes, then cooled and back titrated with standard 0·1N ferrous ammonium sulphate, using N-phenylanthranilic acid or ferroin as indicator. The tellurium is oxidised from the quadri- to the sexavalent stage. Selenium does not interfere.

$$1 \text{ Ml. } N \text{ Ce(SO}_4)_2 \equiv 0{\cdot}06381 \text{ g. Te.}$$

Method B. The solution of tellurous acid or of a tellurite (200 ml.) is treated with 15 ml. of concentrated hydrochloric acid and a measured excess of standard 0·1N potassium dichromate, and allowed to stand for 30 minutes. The residual potassium dichromate is then determined by the addition of excess of standard 0·1N ferrous ammonium sulphate and back titration with 0·1N potassium dichromate, using N-phenylanthranilic acid or ferroin as indicator (see Section **III, 66**). Selenium does not interfere.

$$1 \text{ Ml. } N \text{ K}_2\text{Cr}_2\text{O}_7 \equiv 0{\cdot}06381 \text{ g. Te.}$$

Method C. This is carried out similarly to *Method A* under Selenium (Section **III, 62**). The solution should contain 0·15 to 0·20 g. of tellurous oxide or its equivalent.

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}06381 \text{ g. Te.}$$

III, 81. Determination of thallium.—An iodine chloride indicator is prepared by dissolving a small crystal of iodine in 5 ml. of carbon tetrachloride in a stoppered bottle, adding 50 ml. of concentrated hydrochloric acid and then 0·1N ceric sulphate (Section **III, 74**) dropwise with frequent shaking until the colour of the iodine just disappears from the solvent layer. A measured volume of the thallous solution is then added, and standard 0·1N ceric sulphate run in as before until the carbon tetrachloride again becomes colourless. More hydrochloric acid should be added, if necessary, to maintain its concentration about 5N.

The change is :

$$\text{Tl}^+ - 2\epsilon = \text{Tl}^{+++},$$

whence 1 ml. N Ce $(\text{SO}_4)_2 \equiv 0{\cdot}1022$ g. Tl.

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* Ceric sulphate alone does not oxidise selenite or tellurite, but it oxidises chromium to the sexavalent stage and this, in turn, oxidises tellurite (but not selenite) to the sexavalent condition ; any Cr^{vi} at the end is reduced by the ferrous sulphate. The ceric ion acts as a potential mediator (compare Section **I, 50A**).

Note. Ceric solutions are also available for the analysis of hydrogen peroxide or any per-salts such as persulphates, " perborates " and percarbonates ; also for any ferrous titration where potassium dichromate and potassium permanganate are applicable, and for the determination of tervalent antimony and mercurous mercury.

III, 82. Determination of cerium.—*Method A*. The cerous salt in the form of sulphate in 100 ml. of 1 : 4 sulphuric acid is treated with 2 g. of ammonium sulphate, 1 g. of A.R. sodium bismuthate is added, and the solution heated to boiling. The mixture is cooled somewhat, 50 ml. of 2 per cent sulphuric acid added, filtered through a Gooch, porous porcelain or sintered glass crucible, and washed with 100 to 150 ml. of 2 per cent sulphuric acid.

$$2Ce_2(SO_4)_3 + 2NaBiO_3 + 6H_4SO_4 \\ = 4Ce(SO_4)_2 + Bi_2(SO_4)_3 + Na_2SO_4 + 6H_2O.$$

Excess of 0·025*N* ferrous ammonium sulphate is added (as shown by the change from yellow to colourless, and the consequent complete reduction of the ceric to the cerous salt), and the excess of ferrous salt titrated with 0·1*N* potassium permanganate to the first appearance of a pink colour.

$$1 \text{ Ml. } 0{\cdot}025N\ FeSO_4 \equiv 0{\cdot}003503 \text{ g. Ce.}$$

Method B. 100–300 Ml. of the solution, containing 0·1 to 0·3 g. of cerium and 2·5 to 7·5 ml. of concentrated sulphuric acid, are treated with 1 to 5 g. of A.R. ammonium persulphate and 10 drops of 0·1*N* silver nitrate solution (catalyst), and then boiled for 10 minutes. The solution is cooled to room temperature, and is ready for titration. Two procedures may be used.

(i) Add 10 to 20 ml. of 10 per cent potassium iodide solution, and titrate the liberated iodine with 0·1*N* or 0·025*N* sodium thiosulphate. To avoid the oxidation of the hydriodic acid by the air, the titration should be performed in an atmosphere of carbon dioxide.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}1401 \text{ g. Ce.}$$

(ii) Titrate the solution with 0·1*N* or 0·025*N* ferrous ammonium sulphate, using xylene cyanol FF, *N*-phenylanthranilic acid or ferroin as indicator (Section **III, 75**).

$$1 \text{ Ml. } N\ FeSO_4 \equiv 0{\cdot}1401 \text{ g. Ce.}$$

OXIDATIONS WITH MANGANIC SULPHATE

III, 83. General discussion.—The introduction of aqueous manganic sulphate as a volumetric oxidising agent by A. R. J. P. Ubbelohde (1935) originated in an attempt to improve the poor end points which are sometimes obtained with potassium permanganate solutions, due to the slow rate of oxidation by the permanganate ion and to other causes. It was found that reactions involving only the removal of electrons were more rapid and yielded better end points, for example :

$$Fe^{++} + Mn^{+++} = Fe^{+++} + Mn^{++}.$$

Manganic sulphate solutions gave satisfactory end points in the determination of ferrous salts in the presence of chloride ions (contrast potassium permanganate), nitrites, hydrogen peroxide, oxalates, and vanadous salts.

III, 84. Preparation and standardisation of manganic sulphate solutions.—*Preparation.* This is based upon the oxidation of manganous sulphate with potassium permanganate :

$$8MnSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Mn_2(SO_4)_3 + K_2SO_4 + 8H_2O.$$

Owing to the deep red tint and also the danger of hydrolysis in dilute solutions, it is best to work with *ca.* 0·07*N* solutions prepared in the following manner.

To 50 ml. of a solution of A.R. manganous sulphate (15·1 g. in 1 litre of 6*N* sulphuric acid) add 3 ml. of concentrated sulphuric acid with water-cooling ; then add 12 ml. of 0·5*N* potassium permanganate solution, 2 ml. at a time, at intervals of about 3 minutes. After 8 ml. and after 12 ml. of the permanganate solution have been added, cautiously introduce a further 2 ml. of concentrated sulphuric acid. Store the solution for 4 hours before use. With the above precautions, reduction proceeds smoothly to manganic sulphate, and higher valency stages never accumulate in sufficient concentration to give rise to troublesome precipitates of higher oxides. If larger quantities of the solution are to be prepared, special precautions to ensure adequate cooling are necessary.

The solution of manganic sulphate has a deep red colour. It must be stored in blue bottles and kept in a dark cupboard when not in use. On exposure to light in a clear bottle, a precipitate gradually appears owing to the formation and hydrolysis of quadrivalent manganese salts :

$$2\mathrm{Mn}^{+++} = \mathrm{Mn}^{++} + \mathrm{Mn}^{++++}.$$

Standardisation. This is effected by running the manganic sulphate solution into standard ferrous ammonium sulphate solution (Section **III, 48,** *Procedure D*) ; one drop in excess of the former gives a pink end point with a yellowish tinge. A better pink colouration, particularly for use in artificial light, is obtained on adding 2 drops of syrupy phosphoric acid.

III, 85. Applications of manganic sulphate solutions.—A. Ferrous salts in the presence of chloride ions. Satisfactory results are obtained up to a concentration of hydrochloric acid of N. When the concentration of acid exceeds $0{\cdot}2N$, 0·5 to 1 ml. of syrupy phosphoric acid is added to improve the end point and the titration is carried out slowly and with vigorous shaking.

B. Nitrites. Excellent end points are obtained and the titrations are rapid (contrast Section **III, 58**).

C. Hydrogen peroxide. Manganic sulphate solution reacts almost instantaneously with hydrogen peroxide, and the end point is sharp.

D. Oxalates. Titration is effected at 35°C, and the end point is sharp.

E. Vanadium. Vanadium salts are reduced with liquid zinc amalgam or with amalgamated zinc to the bivalent stage ; the latter solution at 45° to 50°C may be rapidly and satisfactorily oxidised by manganic sulphate solution to the quinquevalent stage. This procedure is superior to the permanganate method (Section **III, 94**).

REDUCTIONS WITH TITANOUS SALTS

III, 86. General discussion.—E. Knecht (1903) first suggested the use of titanous chloride for the determination of iron. This estimation differs from those already described in that the iron is reduced instead of oxidised, for example :

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

The end point of the reaction is judged by the use of an indicator such as methylene blue, which is reduced and decolourised when the titanous solution is present in slight excess, or of ammonium thiocyanate, which remains red as long as any ferric salt is present. The latter is generally preferred because methylene blue is somewhat slow in reaction below about 35°C ; if, however, one drop of 10 per cent sodium salicylate solution is added, the change is instantaneous at the ordinary temperature.

Titanous chloride is a more powerful reducing agent than stannous chloride (compare Table XVI). It is oxidised rapidly in the air and should be kept out of direct sunlight. A. S. Russell (1926) has shown that titanous sulphate in $4N$ sulphuric acid solution is more stable to air than is the chloride (compare ferrous chloride and ferrous sulphate), and, indeed, its titre against potassium permanganate solution when kept in a burette exposed to air remains unchanged for 12 hours. Nevertheless, for accurate work and for requiring a large number of routine determinations, solutions of both titanous chloride and sulphate should be stored in an atmosphere of hydrogen ; titrations, particularly of the chloride, are best carried out in an atmosphere of carbon dioxide.

Formerly titanous salts were employed for numerous quantitative estimations* ; many of these determinations can now be made more simply by other methods. The chief present uses of the reagent are in the estimation of ferric salts, of organic nitro and nitroso compounds, azo dyes, and various routine analyses. Only the first-named falls within the compass of this volume. The reaction with a nitro compound may be written :

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* For complete details, see E. Knecht and E. Hibbert, *New Reduction Methods of Volumetric Analysis*, 1925 (Longmans, Green and Co.), W. M. Thornton, *Titanium*, 1927 (Chemical Catalog Co.).

$$R.NO_2 + 6Ti^{+++} + 6H^+ = R.NH_2 + 6Ti^{++++} + 2H_2O,$$
$$\text{hence } NO_2 \equiv 6Ti^{+++}*.$$

III, 87. Preparation of titanous solutions.—A. Titanous chloride solution. Boil 60 ml. of commercial titanous chloride solution (15 to 20 per cent) for 1 minute with 100 ml. of concentrated hydrochloric acid† in a small flask, allow to cool, and make up to about 2 litres with boiled-out water in the storage bottle (Fig. 2-25). The solution should be thoroughly mixed by shaking and, when freshly prepared, should fill the bottle to the neck ; otherwise air remains, which must be completely displaced by hydrogen.

The burette is first completely filled with the solution. The storage bottle, etc., is connected to a Kipp's apparatus generating hydrogen. The tap of the burette is opened so that the latter is emptied and hydrogen is passed through the system in order to displace the residual air. The tap is now closed, and the burette filled with the solution by suitably rotating the tap. It is now ready for standardisation and for use.

B. Titanous sulphate solution. This is similarly prepared by boiling 60 ml. of commercial titanous sulphate solution (15 to 20 per cent) for 2 to 3 minutes with 200 ml. of 1 : 3 sulphuric acid in a small flask, allowing to cool, and diluting exactly as detailed under titanous chloride.‡ If 3 to 4*N* sulphuric acid is used for dilution, the stability of the solution is considerably increased. Another method, due to A. S. Russell (1926), is to reduce a solution of titanic sulphate in 4*N* sulphuric acid with liquid zinc amalgam (Section **III, 95**) for 1 to 2 minutes, and then to decant the resultant titanous sulphate solution into a storage vessel or flask. This method is particularly valuable when relatively small volumes of the solution are required.

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* For further details, see J. F. Thorpe and M. A. Whiteley, *A Student's Manual of Volumetric Analysis*, 1925 (Longmans, Green and Co.) and W. M. W. M. Cumming, I. V. Hopper and T. S. Wheeler, *Systematic Organic Chemistry*, 1937 (Constable and Co.).

† Commercial titanous chloride solution sometimes contains sulphides, which are eliminated as hydrogen sulphide on boiling.

‡ Callan and Henderson (1920) use a more concentrated solution of titanous sulphate for the titration of nitro and other organic compounds. It is prepared by boiling 300 ml. of commercial titanous sulphate solution (15 to 20 per cent) with 500 ml. of 1 : 3 sulphuric acid for a few minutes, cooling, and making up to 1 litre.

III, 88. Standardisation of the titanous sulphate (or titanous chloride).—A. With pure iron. Weigh out accurately 1·001 g. of A.R. iron wire (assay value 99·9 per cent ; see Section **III, 46**) into a long-necked flask held in an inclined position, or into a conical flask carrying a short funnel in the mouth, and add about 100 ml. of 5*N* sulphuric acid. When all the iron has passed into solution, transfer quantitatively to a 500 ml. volumetric flask, add a further 200 ml. of 5*N* sulphuric acid, and make up to the mark. Shake thoroughly. Pipette 25 ml. of this solution ($\equiv$ 0·0500 g. Fe) into a 250 to 350 ml. conical flask, fitted with a three-holed rubber stopper carrying tubes as described in Section **III, 116B**), and carefully oxidise with potassium permanganate solution of about 0·02*N* strength until a faint pink tinge is obtained. Boil vigorously to expel dissolved oxygen whilst a slow current of carbon dioxide is passed through the flask. Cool the solution, add 10 to 20 ml. of 10 per cent ammonium or potassium thiocyanate solution and run in the titanous sulphate (or chloride) solution until the red colour, due to " ferric thiocyanate," has disappeared. The stream of carbon dioxide is maintained throughout the whole of the operation. The reduction of the last few mg. of the ferric salt is somewhat slow and it is therefore best to add the titanous solution dropwise with intervals of several seconds between the drops when the end point has almost been reached. The use of a large excess of thiocyanate renders the end point much sharper. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, as otherwise the indicator is not sensitive. Repeat the titration with two other 25 ml. portions of the iron solution.

Calculate the weight of iron equivalent to 1 ml. of the titanous solution.

B. With ferrous ammonium sulphate. Weigh out accurately 3·511 g. of A.R. ferrous ammonium sulphate (Section **III, 46**) dissolve it in water, add about 150 ml. of 5*N* sulphuric acid, and make up the solution to 250 ml. in a standard flask. Shake thoroughly. Pipette 25 ml. of this solution ($\equiv$ 0·0500 g. of Fe) into a 250 to 350 ml. conical flask and proceed as described under **A**. This method is less accurate than that employing pure iron (for reasons, see Sections **III, 46** and **III, 48**, *Procedure D*).

A.R. ferric ammonium sulphate (iron alum) may also be used for the standardisation.

III, 89. Determination of iron in an ore.—Weigh out accurately about 2 g. of the iron ore,* dissolve it in 100 ml. of 1 : 1 hydrochloric acid, and make up the solution to 250 ml. in a volumetric flask as described in Section **III, 53.** Pipette 25 ml. of this solution into a 250 ml. conical flask, and precipitate the iron by the addition of ammonium hydroxide solution. Oxidise the ferrous hydroxide by adding excess of pure hydrogen peroxide solution. Boil for 10 minutes to decompose the excess of hydrogen peroxide. Cool, add concentrated hydrochloric acid until the acid content of the solution is about 10 per cent by volume, then 10 ml. of 10 per cent ammonium thiocyanate solution. Titrate against the standardised titanous sulphate (or chloride) solution in an atmosphere of carbon dioxide until the red colour just disappears (Section **III, 88A**). Repeat with two other 25 ml. portions of the solution.

From the results, calculate the percentage of total iron in the sample of ore used.

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*Ridsdale's " Iron Ore, No. 17 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Iron Ore ' A ' " (one of the British Chemical Standards) may be used.

REDUCTIONS WITH AMALGAMATED ZINC AND WITH LIQUID AMALGAMS

III, 90. General discussion.—The use of amalgamated zinc as a reducing agent has been fully dealt with in Section **III, 51B** : full details are given in that Section of the manipulation of the very convenient Jones' reductor. Experimental details, based upon the use of the Jones' reductor, for the determination of uranium, titanium, molybdenum, and vanadium are given below.

Nakazono (1921) introduced liquid zinc amalgam as a reducing agent in volumetric analysis, and subsequent Japanese workers, particularly Someya (1924–1927), have added liquid cadmium, bismuth and lead amalgams. These amalgams have different reduction potentials (see Table XV) ; the order is zinc, cadmium, lead, bismuth, the first-named being the most powerful reductant. The final reduction products obtained with these amalgams for a few elements are collected in the Table.

Liquid Amalgam	*Iron*	*Titanium*	*Molybdenum*	*Vanadium*	*Uranium*	*Tungsten*
Zinc	Fe^{++}	Ti^{+++}	Mo^{+++}	V^{++}	U^{++++}	—
Cadmium	Fe^{++}	Ti^{+++}	Mo^{+++}	V^{++}	U^{++++}	—
Lead	Fe^{++}	Ti^{+++}	Mo^{+++}	V^{++}	U^{++++}	W^{+++}
Bismuth	Fe^{++}	Ti^{+++}	Mo^{+++} *or* Mo^{+++++}*	VO^{++}	U^{++++}	W^{++++}

Zinc amalgam also reduces chromium to Cr^{++}.

In view of the poisonous character of mercury vapour—the effect is a cumulative one—the author prefers to recommend the use of the Jones reductor for most reductions in routine work. However, in determinations, such as those of titanium (with zinc amalgam) and of tungsten (with lead amalgam), liquid amalgams offer certain advantages, and their use for these determinations is accordingly described below (Sections **III, 95, 96**). These Sections incidentally contain the methods of preparation of liquid zinc and lead amalgams ; the amalgams of cadmium and bismuth are prepared similarly to that of zinc, except that for bismuth hydrochloric acid replaces sulphuric acid. Zinc amalgam is useful in the preparation of titanous, vanadous and chromous salt solutions.

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* The exact product depends upon the pH of the solution.

A special apparatus is described for the determination of titanium (Section **III, 95**). For many purposes (e.g., the reduction of ferric salts), however, the reduction may be carried out in a 250 ml. reagent bottle fitted with a well-ground stopper. For the reduction of 50 ml. of a solution of approximately deci-normal concentration, which should be 2 to $4N$ with respect to sulphuric acid, 30 to 50 ml. of amalgam may be used ; the reaction is complete after shaking for a few minutes. The contents of the bottle are then transferred to the titration flask or other vessel, the bottle rinsed 2 or 3 times with small volumes of boiled-out water, the washings being of course added to the flask. The same amalgam can be used many times before it becomes exhausted.

III, 91. Determination of uranium.—The uranium solution (100 ml., about 0·25 g. U) should contain 5 per cent by volume of sulphuric acid, no compounds that are reduced in the Jones reductor, and be free from nitric acid. Add enough $0{\cdot}1N$ potassium permanganate to produce a permanent pink tint, cool the solution to 20° to 25°C, and pass it through a Jones reductor (Section **III, 51B**) at a rate of 50 to 100 ml. per minute. Part of the uranium is reduced below the quadrivalent condition. Bubble a stream of air through the solution for 5 to 6 minutes ; the dirty dark green colour changes to the bright apple-green characteristic of uranous salts. Titrate the solution with standard $0{\cdot}1N$ potassium permanganate. Carry out a blank determination with the reagents in the usual way, and subtract the blank correction from the volume of potassium permanganate required in the estimation.

$$1 \text{ Ml. } N\ KMnO_4 \equiv 0{\cdot}1190 \text{ g. U.}$$

The cold sulphuric acid solution of quadrivalent uranium is stable to air for several hours, and even a rapid stream of air effects no change in 30 minutes.

III, 92. Determination of titanium.—The titanium solution should be free from all metals that are reduced in a Jones reductor and also from all substances which are likely to react subsequently with potassium permanganate. 150 Ml. of the solution, containing sulphuric acid and 0·12 to 0·15 g. of titanium, are treated with enough $0{\cdot}1N$ potassium permanganate to produce a permanent pink tint, and then passed through a Jones reductor (Section **III, 51B**) ; the reduced solution is collected in a five-fold excess of an acidified solution of A.R. ferric alum—100 ml. of a 10 per cent solution suffices for most purposes. The ferrous iron thus produced by reaction with the tervalent titanium is titrated with standard 0·1*N* potassium permanganate. Subtract the blank correction determined in the usual manner.

1 Ml. *N* $KMnO_4$ ≡ 0·04790 g. Ti.

III, 93. Determination of molybdenum.—The molybdenum solution should be free from all metals that are reduced in a Jones reductor, and from all substances which are likely to react subsequently with the potassium permanganate. The cold solution, containing 0·08 to 0·10 g. of molybdenum and 3 to 10 per cent by volume of sulphuric acid, is treated with enough deci-normal potassium permanganate to produce a pink colour, and then passed through a Jones reductor; the reduced solution is collected in a five-fold excess of acidified A.R. iron alum solution (say, 30 ml. of a 10 per cent solution). Add a few ml. of syrupy phosphoric acid to the contents of the receiver and titrate the ferrous sulphate produced with standard 0·1*N* potassium permanganate. Subtract the volume of permanganate required in a blank determination in which the reagents have been carried through all the steps of the process.

1 Ml. *N* $KMnO_4$ ≡ 0·0320 g. Mo.

Note. Owing to the instability of tervalent molybdenum compounds, exposure to air should be reduced to a minimum, and the lower tube of the reductor should pass under the surface of the iron solution.

III, 94. Determination of vanadium.—*Method A.* The experimental details are similar to those described under Titanium (Section **III, 92**). The vanadium solution, containing sulphuric acid, is treated with enough 0·1*N* potassium permanganate to produce a pink colour and is passed through a Jones reductor, whereupon it is reduced to the bivalent stage; the reduced solution is caught in excess of an acidified solution of A.R. iron alum, and the ferrous iron thus formed is titrated with standard 0·1*N* potassium permanganate. Actually, the ferric salt oxidises the vanadous salt only to the quadrivalent condition, which is stable in air, and the final oxidation to the quinquevalent state is completed somewhat slowly by the potassium permanganate. The titration is somewhat slow towards the end, but the final point is quite definite; by heating the solution to 70° to 80°C towards the end of the titration, the oxidation is rapid.

1 Ml. *N* $KMnO_4$ ≡ 0·01698 g. V.

Method B. The vanadium solution should contain 2 per cent by volume of sulphuric acid, and be free from arsenic, antimony, iron, chromium and other substances that are oxidised by potassium permanganate after reduction with sulphur dioxide. Heat the solution to boiling, add a strong solution of potassium permanganate until the solution is pink, fit the flask with wash bottle tubes, and pass sulphur dioxide through the solution for 5 to 10 minutes ; the solution acquires a pure blue colour (vanadyl sulphate) and is quite stable in the presence of sulphuric acid. Next pass a rapid stream of carbon dioxide through the boiling solution until it is free from sulphur dioxide, as tested by bubbling the issuing gas through an acidified and very dilute solution of potassium permanganate. Cool the solution to 60° to 80°C, and titrate with standard 0·1*N* potassium permanganate.

$$2H_3VO_4 + H_2SO_3 + H_2SO_4 = 2(VO)SO_4 + 5H_2O\ ;$$

$$5V_2O_2^{++++} + 2MnO_4^- + 22H_2O = 10H_3VO_4 + 2Mn^{++} + 14H^+.$$

$$1\ \text{Ml.}\ N\ KMnO_4 \equiv 0{\cdot}05095\ \text{g. V.}$$

Note. Since sulphur dioxide does not reduce molybdic acid, this procedure can be employed in the presence of molybdenum. Both molybdic and vanadic acids are reduced in the Jones reductor, hence the former may be determined by reducing both with amalgamated zinc and making allowance for the vanadium present.

III, 95. Determination of titanium (zinc amalgam method) —This method is based upon the use of liquid zinc amalgam as the reducing agent, whereby the titanium is quantitatively reduced to the tervalent state ; the latter is titrated against standard ferric ammonium sulphate solution with potassium thiocyanate solution as indicator.

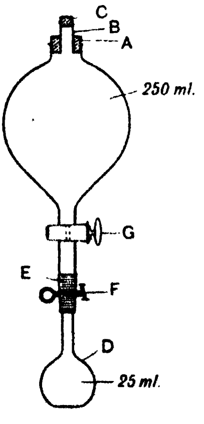


FIG. 3-7.

The apparatus employed for the titration is shown in Fig. 3-7. A 250 ml. globular separating funnel is closed with a rubber stopper **A** carrying a piece of 0·25 inch tubing **B,** which is closed by a small cork **C.** (Alternatively, the funnel may be closed with a three-holed rubber stopper carrying inlet and outlet tubes for carbon dioxide and a small stopper in the third hole.) The lower end of the funnel is connected by means of thick-walled ("pressure") tubing **E** to a 25 ml. flask **D** (this may consist of a 25 ml. volumetric flask, etc.) ; **F** is a pinch cock. A sample of the substance, equivalent to 0·1 to 0·2 g. of TiO_2 (1), is digested with 20 ml. of concentrated sulphuric acid and 15 g. of powdered A.R. ammonium sulphate until it is entirely dissolved. Bulb **D** and the rubber tubing, etc., to the stop-cock **G** are filled with cooled, freshly boiled distilled water containing 1 per cent of sulphuric acid (" acid distilled water "), and **F** and **G** are closed. Fifteen ml. of liquid zinc amalgam are placed in the funnel and the cooled sample is transferred to the funnel using about 75 ml. of " acid distilled water." Several grams of A.R. sodium bicarbonate (preferably in the form of two tablets) are added, and stopper **A** is inserted with cork **C** removed. When the gas evolution has ceased, a further few grams of A.R. sodium bicarbonate are added through **B.** When effervescence ceases, cork **C** is immediately replaced and the whole apparatus vigorously shaken for 5 minutes. The funnel is then supported in a stand, **G** and **F** are opened, and the amalgam is allowed to flow into **D** : this is best accomplished by alternatively squeezing and releasing the tube **E** with the fingers. When the last particles of amalgam have dropped into the flask, **G** and **F** are closed, and bulb **D** is disconnected for convenience whilst titrating. Stopper **C** is removed, and 5 ml. of saturated potassium thiocyanate solution added through **B** by means of a pipette. Stopper **A** is removed and both tube and stopper are washed into the funnel with " acid distilled water." The solution is then titrated in the funnel with the ferric ammonium sulphate solution (2). It is important to add the latter solution very rapidly until the first appearance of a wine-red colour. Stop-cock **G** is then opened, and tube **E** squeezed several times to force its liquid into the funnel ; this will cause the red colour to disappear. The titration is then completed by adding the ferric solution drop by drop to the end point.

The **ferric ammonium sulphate solution** is approximately 0·07*N* and is **prepared** by dissolving *ca.* 30 g. of the A.R. salt in a mixture of 300 ml. of water and 10 ml. of concentrated sulphuric acid ; potassium permanganate solution is added dropwise as long as the pink colour disappears (if at all), and the solution is then diluted to 1 litre. The solution is *standardised,* after reduction with zinc amalgam in the above apparatus, by titration against standard 0·1*N* potassium permanganate.

The **zinc amalgam** is **prepared** by washing 15 g. of pure, fine-mesh zinc (*e.g.*, A.R.) with dilute sulphuric acid, and then heating for 1 hour on the water bath with 300 g. of mercury plus 5 ml. of 1 : 4 sulphuric acid. (**Caution.** Mercury vapour is highly poisonous; the operation must therefore be performed in a fume cupboard provided with a good draught.) The whole is allowed to cool, the amalgam washed several times with dilute sulphuric acid, and the liquid portion separated from the solid by means of a separating funnel. The solid is reserved for another preparation of the amalgam. The liquid amalgam is preserved under dilute sulphuric acid ; reaction with the latter is very slow, and the same sample of amalgam may be employed for several reductions.

Notes. 1. This method is of particular value for the determination of titanium in pigments and similar products. Calcium sulphate does not interfere with the subsequent reduction because its precipitation is prevented by the high concentration of sulphuric acid. Barium sulphate should be removed by filtration before the reduction of the titanium. If two determinations are carried out, and in one case the reduced solution be titrated with the ferric solution and potassium thiocyanate, and in the other case by standard $0{\cdot}1N$ potassium permanganate (this gives Ti + Fe), the method may be employed for the **determination of iron and titanium in admixture.**

2. For the most accurate results it is best to insert the three-holed rubber stopper referred to above, and to conduct the titration in an atmosphere of carbon dioxide.

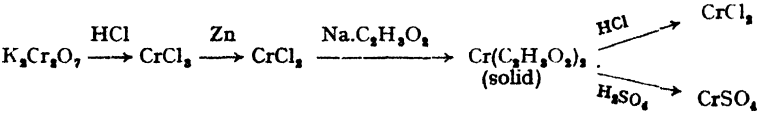
3. It is advisable to run a blank to determine how much ferric solution is required to give an end point in a volume of 3 per cent sulphuric acid equal in volume to that of the final solution and containing 5 ml. of saturated potassium thiocyanate solution.

III, 96. Determination of tungsten.—This element is not reduced to any definite valency stage in the Jones reductor. Lead amalgam reduces tungsten as tungstate to the tervalent condition (W_2O_3) in strong hydrochloric acid at 50°C in an atmosphere of carbon dioxide (K. Someya, 1925). This is titrated with standard $0{\cdot}1N$ potassium permanganate in the presence of concentrated manganous sulphate solution ; it is thereby oxidised to the WO_3 stage, when 3 equivalents of $KMnO_4$ are equivalent to 1 mol of WO_3.

The **lead amalgam is prepared** by washing pure lead with concentrated hydrochloric acid (to remove the film of oxide), and then heating with pure mercury in a casserole until a homogeneous liquid is produced. This process should be carried out in a fume cupboard provided with a very efficient draught. The amalgam is allowed to cool, washed with cold distilled water, and the solid removed in a separating funnel by appropriately manipulating the tap.

III, 97. REDUCTIONS WITH CHROMOUS SALTS.

Chromous solutions are more powerful reducing agents than titanous salts, and their application to volumetric analysis has recently been widely studied, particularly by Zintl and his co-workers (1927 →). The chromous solution is best prepared by the following series of changes :



$$\begin{tikzcd}[column sep=small] & & & & CrCl_2 \\ K_2Cr_2O_7 \arrow[r, "HCl"] & CrCl_3 \arrow[r, "Zn"] & CrCl_2 \arrow[r, "Na.C_2H_3O_2"] & \underset{\text{(solid)}}{Cr(C_2H_3O_2)_2} \arrow[ur, "HCl"] \arrow[dr, "H_2SO_4"'] & \\ & & & & CrSO_4 \end{tikzcd}$$

Chromous solutions are readily oxidised by air, hence precautions must be taken in their preparation, storage and use to exclude oxygen. A suitable apparatus for storing these solution is shown in Fig. 2-25 or 2-26. End points are usually determined by potentiometric titration. The solutions are standardised against pure copper sulphate or pure potassium dichromate.

The reagent may be employed *inter alia* for the determination of copper, mercury, silver, gold, stannic tin, bismuth, iron, molybdenum and titanium, and also for the following mixtures by a single titration : copper-mercury, copper-silver, copper-iron, copper-tin, gold-copper-silver and gold-copper-mercury*·

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* For further details, the reader is referred to W. Böttger-R. E. Oesper, *Newer Methods of Volumetric Chemical Analysis*, 1938, pp. 131–152 (D. Van Nostrand Company : Chapman and Hall).

III, 98. REDUCTIONS WITH VANADOUS SALTS

Vanadous salts are more powerful reducing agents than titamous salts but less powerful than the corresponding chromous salts. Their introduction to volumetric analysis proper is due to A. S. Russell (1926), who prepared a solution of vanadous sulphate by reducing aqueous vanadic sulphate with liquid zinc amalgam and showed that the solution in $4N$ sulphuric acid is stable for about 1 hour in an open burette. However, precautions should be taken to exclude oxygen in all work with vanadous salts.

K. Maass (1934) prepared the reagent by the electrolytic reduction of ammonium vanadate in the presence of dilute hydrochloric or sulphuric acid, and applied it to the potentiometric titration of ferric iron, copper, and silver, and to mixtures of copper-silver, copper-iron, iron-silver, and iron-vanadium.

P. C. Banerjee (1935) employed a solution of vanadous ammonium sulphate, prepared by the electrolytic reduction of aqueous vanadic sulphate in the presence of ammonium sulphate, and standardised it against a ferric solution in the presence of thiocyanate as indicator. This solution is considered more stable than a vanadous sulphate solution, and was employed for the determination of ferric iron, copper, and chromates.

OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE—IODIMETRY AND IODOMETRY

III, 99. General discussion.—**Iodimetry** covers titrations *with* a standard solution of iodine. **Iodometry** deals with the titration *of* iodine liberated in chemical reactions. The normal oxidation potential of the reversible system :

$$I_2 + 2\epsilon \rightleftharpoons 2I^-,$$

is 0·535 volt. This shows that iodine is a much weaker oxidising agent than potassium permanganate, potassium dichromate and ceric sulphate (compare Table XVI). Strong reducing agents (substances with a much lower oxidation potential), such as stannous chloride, sulphurous acid, hydrogen sulphide, and sodium thiosulphate, react completely and rapidly with iodine even in acid solution. With somewhat weaker reducing agents, *e.g.*, trivalent arsenic, trivalent antimony and ferrocyanide, complete reaction occurs only when the solution is kept neutral or very faintly acid ; under these conditions the oxidation potential of the reducing agent is a minimum or its reducing power is a maximum. The equations for some of the reactions are given below :

$$\begin{aligned}
Sn^{++} + I_2 &= Sn^{++++} + 2I^- ;\\
SO_3^{--} + I_2 + H_2O &= SO_4^{--} + 2H^+ + 2I^- ;\\
H_2S + I_2 &= S + 2H^+ + 2I^- ;\\
2S_2O_3^{--} + I_2 &= S_4O_6^{--} + 2I^- ;\\
H_3AsO_3 + I_2 + H_2O &\rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-.
\end{aligned}$$

If a strong oxidising agent is treated in neutral or (more usually) acid solution with a large excess of iodide ion, the latter reacts as a reducing agent and the oxidant will be quantitatively reduced. In such cases, an equivalent amount of iodine is liberated, and is then titrated with a standard solution of a reducing agent, which is usually sodium thiosulphate. Examples of such titrations are illustrated by the following equations :

$$\begin{array}{llllll}
2MnO_4^- & +16H^+ & + 10I^- & = 2Mn^{++} & + 5I_2 + 8H_2O ;\\
Cr_2O_7^{--} & +14H^+ & + 6I^- & = 2Cr^{+++} & + 3I_2 + 7H_2O ;\\
H_2O_2 & + 2H^+ & + 2I^- & = 2H_2O & + I_2 ;\\
BrO_3^- & + 6H^+ & + 6I^- & = Br^- & + 3I_2 + 3H_2O ;\\
IO_3^- & + 6H^+ & + 5I^- & = 3I_2 + 3H_2O ; &
\end{array}$$

$$
\begin{array}{llllll}
\mathrm{ClO_3^-} & + \mathrm{6H^+} & + \mathrm{6I^-} & = \mathrm{Cl^-} & + \mathrm{3I_2} + \mathrm{3H_2O}\,; \\
\mathrm{ClO^-} & + \mathrm{2H^+} & + \mathrm{2I^-} & = \mathrm{Cl^-} & + \mathrm{I_2} + \mathrm{H_2O}\,; \\
\mathrm{IO_4^-} & + \mathrm{8H^+} & + \mathrm{7I^-} & = \mathrm{4I_2} & + \mathrm{4H_2O}\,; \\
\mathrm{2HNO_2} & + \mathrm{2H^+} & + \mathrm{2I^-} & = \mathrm{2NO} & + \mathrm{I_2} + \mathrm{2H_2O}; \\
\mathrm{2Ce^{++++}} & + \mathrm{2I^-} & & = \mathrm{2Ce^{+++}} & + \mathrm{I_2}\,; \\
\mathrm{2Cu^{++}} & + \mathrm{4I^-} & & = \mathrm{Cu_2I_2} & + \mathrm{I_2}\,; \\
\mathrm{Cl_2} & + \mathrm{2I^-} & & = \mathrm{2Cl^-} & + \mathrm{I_2}\,; \\
\mathrm{Br_2} & + \mathrm{2I^-} & & = \mathrm{2Br^-} & + \mathrm{I_2}.
\end{array}
$$

The normal oxidation potential of the iodine-iodide system is independent of the *p*H of the solution so long as the latter is less than about 8 ; at lower acidities iodine reacts with hydroxyl ions to form iodide and the extremely unstable hypoiodite, the latter being transformed rapidly into iodate and iodide by self oxidation and reduction :

$$
\begin{array}{rl}
\mathrm{I_2} + \mathrm{2OH^-} & = \mathrm{I^-} + \mathrm{IO^-} + \mathrm{H_2O}\,; \\
\mathrm{3IO^-} & = \mathrm{2I^-} + \mathrm{IO_3^-}.
\end{array}
$$

It has been shown in Section **I, 56** that the oxidation potentials of certain substances increase considerably with increasing hydrogen ion concentration of the solution. This is the case with systems containing permanganate, dichromate, arsenate, antimonate, bromate, etc., *i.e.*, with anions which contain oxygen and therefore require hydrogen for complete reduction. Many weak oxidising anions are completely reduced by iodide ions if their oxidation potentials are raised considerably by the presence in solution of a large amount of acid.

By suitable control of the *p*H of the solution, it is sometimes possible to titrate the reduced form of a substance with iodine, and the oxidised form after the addition of iodide with sodium thiosulphate. Thus with the arsenite-arsenate system :

$$\mathrm{H_3AsO_3} + \mathrm{I_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3AsO_4} + \mathrm{2H^+} + \mathrm{2I^-},$$

the reaction is completely reversible. At *p*H values between 4 and 9, arsenite can be titrated with iodine solution. In strongly acid solutions, however, arsenate is reduced to arsenite and iodine is liberated. Upon titration with sodium thiosulphate solution, the iodine is removed and the reaction proceeds from right to left.

With certain weak oxidising agents, complete reduction with the iodide ion may be difficult ; the reaction may be made suitable for quantitative work by one of the following methods ;

(i) Increase of the iodide ion concentration, as for the reaction :

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2.$$

(ii) Increase of the hydrogen ion concentration if this increases the oxidation potential of the system.

(iii) The iodine may be removed from the sphere of reaction either by boiling and then collecting in an appropriate solvent, or it may be extracted with an immiscible solvent, such as chloroform, carbon tetrachloride or carbon disulphide.

(iv) If the reaction is a slow one in an acid medium, it is advisable to replace the air in the titration vessel by carbon dioxide (this is most simply effected by the addition of 2 or 3 half-gram portions of pure sodium bicarbonate). This is because the velocity of the reaction :

$$4I^- + 4H^+ + O_2 = 2I_2 + 2H_2O,$$

which is extremely slow in a neutral medium, increases with increasing pH of the solution ; it is greatly accelerated by sunlight and by various catalysts as, for example, traces of copper.

In a number of cases, as in the analysis of the higher oxides of manganese and of lead, it is necessary to boil the oxidising agent with hydrochloric acid or hydrobromic acid, and to pass the liberated chlorine or bromine into excess of potassium iodide solution. Direct boiling of the sample with an acid iodide solution is not advisable, since the latter is a much stronger reducing agent than chloride or bromide and will react with ferric iron, which is a common impurity in these oxides.

$$\begin{aligned} MnO_2 + 4H^+ + 4Cl^- &= Mn^{++} + Cl_2 + 2Cl^- + 2H_2O ; \\ Cl_2 + 2I^- &= 2Cl^- + I_2 ; \\ 2Fe^{+++} + 2I^- &\rightleftharpoons 2Fe^{++} + I_2. \end{aligned}$$

III, 100. Detection of the end point.—A solution of iodine in aqueous iodide has an intense yellow to brown colour. One drop of 0·1*N* iodine solution imparts a perceptible pale yellow colour to 100 ml. of water, so that in otherwise colourless solutions iodine can serve as its own indicator. The test is made much more sensitive by the use of a solution of starch as indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue coloured adsorption complex containing both iodine and iodide, which is visible at very low iodine concentrations. Thus 100 ml. of water containing 0·05 to 0·1 g. of potassium iodide and a few ml. of 0·5 to 1 per cent starch solution becomes distinctly blue upon the addition of 1 drop of $0{\cdot}1N$ iodine. The sensitivity of the starch reaction corresponds to an iodine concentration of 1 to $2 \times 10^{-5}N$ at about 20° C in the presence of a small amount of iodide ($>0{\cdot}001N$). The reaction is less sensitive in the absence of iodide and also decreases in sensitivity with increasing temperature of the solution ; thus at 50°C it is about 10 times less sensitive than at 25°C.

In recent years, carbon tetrachloride has been used in certain reactions instead of starch solution. One litre of water at 25°C will dissolve 0·335 g. of iodine, but the same volume of carbon tetrachloride will dissolve about 28·5 g. Iodine is therefore about 85 times as soluble in carbon tetrachloride as it is in water (compare distribution coefficient in Section **I, 71**), and the carbon tetrachloride solution is highly coloured. When a little carbon tetrachloride is added to an aqueous solution containing iodine and the solution well shaken, the great part of the iodine will dissolve in the carbon tetrachloride ; the latter will fall to the bottom since it is immiscible with water, and the colour of the organic layer will be much deeper than that of the original aqueous solution. The reddish-violet colour of iodine in carbon tetrachloride is visible in very low concentrations of iodine ; thus on shaking 5 ml. of carbon tetrachloride with 50 ml. of $2 \times 10^{-5}N$ iodine, a distinct violet colouration is produced in the organic layer. This enables us to carry out many iodometric determinations with comparative ease. The reaction takes place in 250 ml. glass-stoppered bottles or flasks with accurately ground stoppers. After adding the excess of potassium iodide solution and 5 to 10 ml. of carbon tetrachloride to the reaction mixture, the titration with sodium thiosulphate is commenced. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Towards the end of the titration the bottle or flask is stoppered and shaken after each addition of sodium thiosulphate solution ; the end point is reached when the carbon tetrachloride just becomes colourless. Equally satisfactory results can be obtained with chloroform.

The end point can also be determined potentiometrically (Section **I, 51**).

In iodimetry and iodometry the following solutions *inter alia* are used : iodine, sodium thiosulphate, sodium arsenite, potassium iodate, potassium bromate, and chloramine-T. All of these will be discussed in the ensuing pages. Mention must, however, now be made of the use of a **standard solution containing potassium iodate and potassium iodide.** The latter is quite stable and yields iodine when treated with acid :

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O\,;$$

or $$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O.$$

The standard solution is prepared by dissolving a weighed amount of pure potassium iodate in a solution of potassium iodide, and diluting to a definite volume. This solution has two important uses. The first as a source of iodine in titrations ; it must be added to a solution containing strong acid, but it cannot be employed in a medium which is neutral or possesses a low acidity. The second is in the determination of the acid content of solutions. If excess of the neutral solution of iodate and iodide is added to a dilute solution of a strong acid, the hydrogen ions of the latter yield an equivalent amount of iodine, which can be titrated with standard sodium thiosulphate solution. This method is particularly useful in the titration of very dilute solutions of strong acids, because the end point is readily determined. It is not very satisfactory for weak acids owing to the slowness of the reaction in solutions of low acidity ; results may, however, be obtained by adding an excess of sodium thiosulphate solution after the addition of the iodate-iodide mixture, and then back-titrating the excess of thiosulphate with standard iodine solution.

III, 101. Preparation of 0·1*N* sodium thiosulphate.—*Discussion.* Sodium thiosulphate $Na_2S_2O_3,5H_2O$ is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard.* It is a reducing agent by virtue of the reaction :

$$2S_2O_3^{--} \rightarrow S_4O_6 + 2\epsilon\,;$$

the equivalent weight of sodium thiosulphate pentahydrate is its molecular weight, or 248·20†. An approximately 0·1*N*

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* A.R. sodium thiosulphate has a purity of 99 to 101 per cent.

† The same result is deduced from the equations :

$$I_2 + 2\epsilon = 2I^-,$$

and $$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Alternatively, sodium thiosulphate may be regarded as interacting with weak oxidising agents in accordance with the equation :

$$2Na_2S_2O_3 + O + H_2O = Na_2S_4O_6 + 2NaOH.$$

This leads to the same result, *viz.*, the equivalent weight is 1 mol.

solution is prepared by dissolving about 25 g. of A.R. crystallised sodium thiosulphate in 1 litre of water in a volumetric flask. The solution is standardised by any of the methods described below.

Before dealing with these, it is necessary to refer briefly to the stability of thiosulphate solutions. Solutions prepared with conductivity (equilibrium) water are perfectly stable. However, ordinary distilled water usually contains an excess of carbon dioxide ; this may cause a slow decomposition to take place with the formation of sulphur :

$$S_2O_3^{--} + H^+ \rightarrow HSO_3^- + S.$$

Moreover, decomposition may also be caused by bacterial action (*thiobacillus thioparus*), particularly if the solution has been standing for some time. For these reasons, it is recommended :

(i) to prepare the solution with recently-boiled distilled water ;

(ii) to add 3·8 g. of borax or 0·1 g. of anhydrous sodium carbonate per litre ; this serves the double purpose of preventing the above decomposition and helping to keep the solution sterile ;

(iii) exposure to light should be avoided, as this hastens decomposition.

The standardisation of thiosulphate solutions may be effected with potassium iodate, potassium bromate, potassium permanganate, potassium dichromate, copper, or iodine. Owing to the volatility of iodine and the difficulty of preparation of perfectly pure iodine, this method is not a suitable one for beginners. If, however, a standard solution of iodine (see Sections **III, 103, 104**) is available, this may be used for the standardisation of thiosulphate solutions.

Preparation and use of starch solution. Make a paste of 1 g. of soluble starch with a little water, and pour the paste, with constant stirring, into 100 ml. of boiling water, and boil for 1 minute. Allow the solution to cool, and add 3 g. of potassium iodide. This solution may be preserved for a long period if kept under a layer of toluene in a stoppered bottle.

A starch solution which *keeps almost indefinitely* may be prepared by dissolving 1 g. of soluble starch and 0·5 g. of pure salicylic acid in 200 ml. of water. It is best, as a general rule, to confine the use of this indicator to elementary work owing to the possibility of the preservative reacting with one of the reacting substances. If, however, it has been ascertained that the salicylic acid causes no interference in the particular reaction under study, then the starch-salicylic acid indicator may, of course, be used*.

If soluble starch is not available, grind 1 g. of ordinary starch with a little cold water, pour the paste slowly into 100 ml. of boiling water, and boil the solution for 2 minutes. Cool by placing into cold water, and filter the cold solution. This solution cannot safely be kept for more than about a day.

Only freshly prepared or properly preserved starch solution should be used. Two ml. of a 1 per cent solution per 100 ml. of the solution to be titrated is a satisfactory amount ; the same volume of starch solution should always be added in a titration. In the titration of iodine, starch must not be added until just before the end point is reached. Apart from the fact that the fading of the iodine colour is a good indication of the approach of the end point, if the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end point. The indicator blank is negligibly small in iodimetric and iodometric titrations of $0{\cdot}1N$ solutions ; with more dilute solutions, it must be determined in a liquid having the same composition as the solution titrated has at the end point.

Starch solution cannot be employed in alcoholic solution, nor can it be used in a strongly acid medium because hydrolysis of the starch occurs.

Procedure. Weigh out 25 g. of A.R. sodium thiosulphate $Na_2S_2O_3{,}5H_2O$, dissolve it in boiled-out distilled water, and make up to 1 litre with the same water. Add 3·8 g. of borax or 0·1 g. of anhydrous sodium carbonate to stabilise the solution. Shake well.

III, 102. Standardisation of sodium thiosulphate solutions. —A. With potassium iodate. A.R. potassium iodate has a purity of at least 99·9 per cent : it can be dried at 120°C. This reacts with potassium iodide in acid solution to liberate iodine :

$$KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O.$$

Its equivalent weight as an oxidising agent is 1/6 mol or 214·02/6 ; a $0{\cdot}1N$ solution therefore contains 3·567 g. of potassium iodate per litre.

Weigh out accurately 0·14 to 0·15 g. of pure dry potassium iodate, dissolve it in 25 ml. of cold, boiled-out distilled water, add 2 g. of iodate-free potassium iodide* and 5 ml. of 2*N* sulphuric acid (1). Titrate the liberated iodine against the thiosulphate solution with constant stirring. When the colour of the liquid has become a pale yellow, dilute to *ca.* 200 ml. with distilled water, add 2 ml. of starch solution, and continue the titration until the colour changes from blue to colourless. Repeat with two other similar portions of potassium iodate.

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* Alternatively, the addition of 0·1 g. of thymol to 100 ml. of boiling water before mixing with 1 g. of starch produces a starch solution which keeps for several months [Saville, 1941].

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N \text{ Na}_2\text{S}_2\text{O}_3 \equiv 0{\cdot}03567 \text{ g. KIO}_3.$$

Note. 1. Potassium iodate has a small equivalent weight (35·67) so that the error in weighing 0·14 to 0·15 g. may be appreciable. In this case it is better to weigh out accurately 3·567 g. of the A.R. salt (if a slightly different weight is used, the exact normality is calculated), dissolve it in water, and make up to 1 litre in a volumetric flask. 25 Ml. of this solution are treated with excess of pure potassium iodide (1 g. of the solid or 10 ml. of 10 per cent solution), followed by 3 ml. of 2*N* sulphuric acid, ~~and the liberated iodine~~ is titrated as detailed above. The titrations are repeated until two agree within 0·1 ml.; not more than three titrations should be necessary. The normality of the sodium thiosulphate solution is then calculated (see Section **III, 4A**).

B. With potassium bromate. Potassium bromate is very similar in properties to potassium iodate; its only advantage over the latter is that it is less expensive. A.R. potassium bromate has a purity of at least 99·9 per cent. It may be dried at 120° to 150°C, and its aqueous solution is stable. The substance reacts with potassium iodide in acid solution in accordance with the equation:

$$\text{KBrO}_3 + 6\text{KI} + 6\text{HCl} = \text{KBr} + 6\text{KCl} + 3\text{I}_2 + 3\text{H}_2\text{O}.$$

The equivalent weight as an oxidising agent is 1/6 mol; a 0·1*N* solution therefore contains 167·02/60 or 2·784 grams of potassium bromate per litre.

Weigh out accurately 0·11 to 0·12 g. of pure dry potassium bromate (1). Dissolve it in 35 ml. of boiled-out distilled water, add 2 g. of iodate-free potassium iodide, and 5 ml. of 4*N* hydrochloric acid (2). Titrate with the sodium thiosulphate solution until most of the liberated iodine has reacted, dilute with 150 ml. of distilled water, then add 2 ml. of freshly prepared [illegible]ch solution, and complete the titration.

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* The absence of iodate [illegible] indicated by adding dilute sulphuric acid when no immediate yellow coloura[illegible]on should be obtained. If starch is added, no immediate blue colouration should be produced.

Repeat the determination with two further similar samples of potassium bromate.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N \text{ } Na_2S_2O_3 \equiv 0{\cdot}02784 \text{ g. } KBrO_3.$$

Notes. 1. It is better to prepare a 0·1*N* solution by weighing out 2·784 g. of A.R. potassium bromate, dissolving it in water, and making up to 1 litre in a volumetric flask (compare Note I under *A*). 25 Ml. of this solution are treated with excess of pure potassium iodide (1·5 g. of the solid or 15 ml. of the 10 per cent solution), followed by 4 to 5 ml. of 4*N* hydrochloric acid, and the liberated iodine titrated as detailed above. The titrations are repeated until two agree within 0·1 ml.; not more than three titrations should be necessary. The normality of the sodium thiosulphate solution is then calculated.

2. A higher acidity is required than for potassium iodate solutions. The reaction is somewhat slower; the addition of a few drops of 3 per cent ammonium molybdate solution considerably increases the velocity of the reaction.

C. With potassium permanganate. This method is satisfactory provided the experimental conditions given below are strictly followed. Upon adding potassium permanganate to an acid solution containing potassium iodide, the following reaction occurs:

$$2KMnO_4 + 10KI + 16HCl = 12KCl + 2MnCl_2 + 5I_2 + 8H_2O.$$

Measure out 25 ml. of standard 0·1*N* potassium permanganate into a 350 ml. conical, preferably glass-stoppered, flask containing a solution of 6 g. of potassium iodide in 50 ml. of water and 2 ml. of concentrated hydrochloric acid. Allow to stand in the dark for 10 minutes. Titrate the iodine that has been set free with the sodium thiosulphate solution until the solution has a faint straw colour, add 2 ml. of the starch solution, and continue the titration until the blue colour is just destroyed. Carry out a blank determination, but substitute 25 ml. of water for the 25 ml. of the potassium permanganate solution; subtract the volume of thiosulphate solution required in the blank run from that consumed in the other titration. Repeat the determination with two other 25 ml. portions of the permanganate solution.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N \text{ } Na_2S_2O_3 \equiv 0{\cdot}03161 \text{ g. } KMnO_4.$$

D. With potassium dichromate. Potassium dichromate is reduced by an acid solution of potassium iodide to a green chromic salt, and an equivalent weight of iodine is set free:

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 3I_2 + 7H_2O.$$

This reaction is subject to a number of errors: (1) it is not instantaneous, and (2) the hydriodic acid (from excess of iodide and acid) is readily oxidised by air, especially in the presence of chromic salts. It is accordingly best to pass a current of carbon dioxide through the reaction flask before and during the titration (a more convenient but less efficient method is to add some solid sodium bicarbonate to the acid solution, and to keep the flask covered as much as possible), and to allow 5 minutes for its completion.

Place 100 40 ml. of cold, recently-boiled distilled water in a 500 ml. conical, preferably glass-stoppered, flask, add 3 g. of iodate-free potassium iodide and 2 g. 1g of pure sodium bicarbonate, and shake until the salts dissolve. Add 6 ml. of concentrated hydrochloric acid slowly whilst gently rotating the flask in order to mix the liquids; run in 25 ml. of standard $0{\cdot}1N$ potassium dichromate (1), mix the solutions well, and wash the sides of the flask with a little boiled-out water from the wash bottle. Stopper the flask (or cover it with a small watch glass), and allow to stand in the dark for 5 minutes in order to complete the reaction. Rinse the stopper or watch glass, and dilute the solution with 300 ml. of cold, boiled-out water. Titrate the liberated iodine against the sodium thiosulphate solution contained in a burette, whilst constantly rotating the liquid so as to thoroughly mix the solutions. When most of the iodine has reacted as indicated by the solution acquiring a yellowish-green colour, add 2 ml. of starch solution and rinse down the sides of the flask; the colour should change to a shade of blue. Continue the addition of the thiosulphate solution dropwise, and swirling the liquid constantly, until 1 drop changes the colour from greenish-blue to light green. The end point is sharp, and is readily observed in a good light against a white background. Carry out a blank determination, substituting distilled water for the potassium dichromate solution; if the potassium iodide is iodate-free, this should be negligible. Repeat with two other 25 ml. portions of the dichromate solution.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}04904 \text{ g. } K_2Cr_2O_7.$$

Note. 1. If preferred, about 0·2 g. of A.R. potassium dichromate may be accurately weighed out, dissolved in 50 ml. of cold, boiled-out water, and the titration carried out as detailed above.

E. With copper. This method is not recommended except where the thiosulphate solution is to be used for the determination of copper. A.R. copper turnings (prepared from electrolytic copper) has a purity of over 99·9 per cent.*

Weigh out accurately about 0·25 g. of pure copper turnings into a 250 to 350 ml. conical flask, and dissolve it in a mixture of 3 ml. of concentrated nitric acid and 6 ml. of water. Dilute to 25 ml. with water, heat the solution to boiling, add 0·5 g. of urea and boil the solution for 1 to 2 minutes. The urea completely eliminates nitrous acid and oxides of nitrogen, which interfere with the determination.† Cool the solution, and add 6*N* ammonium hydroxide solution slowly until a slight permanent precipitate of cupric hydroxide just forms. Add 5 ml. of glacial acetic acid to the almost neutral solution. Cool the solution, and add 3 g. of potassium iodide dissolved in 30 ml. of water (or 30 ml. of a 10 per cent solution), cover the conical flask with a watch glass, and allow to stand for 1 minute. Titrate the liberated iodine with the thiosulphate solution, added from a burette, until the brown colour due to iodine has changed to light yellow. Add 2 ml. of starch solution, and continue the titration with the thiosulphate, stirring constantly, until 1 drop changes the colour from blue to yellowish-white.‡ The cuprous iodide is always coloured by adsorbed " starch iodide," and is not a pure white at the end point. Repeat the determination with two other 0·25 g. portions of copper.

When starch alone is employed as indicator, the iodine is not completely available for reaction with the sodium thiosulphate and hence the strength of the thiosulphate solution determined by means of copper is slightly higher (*ca.* 3 per cent) than that standardised against potassium iodate or iodine. It is for this reason that the method was not recommended above except where the thiosulphate solution is

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* The Bureau of Analysed Samples Ltd., of Middlesbrough, England, supply copper turnings of 99·91 per cent purity (a " British Chemical Standard ").

† Nitrite and nitric oxide when present even in minute quantities interfere. Thus nitrite in acid solution reacts in accordance with the equation :

$$2NO_2^- + 2I^- + 4H^+ = 2NO + I_2 + 2H_2O.$$

The nitric oxide is oxidised by air to nitrogen peroxide, which reacts with the iodide to form more nitric oxide and iodine ; the cycle is then repeated. For this reason, if a trace of nitric oxide is present in the solution, no permanent end point is obtained upon titration with thiosulphate solution in the presence of starch. The colour returns rapidly upon the removal of the iodine.

‡ The end point is rendered sharper by adding 1 or 2 drops of 0·1*N* silver nitrate ; the yellowish colour of silver iodide neutralises the purplish tinge of cuprous iodide.

subsequently to be used for the determination of copper.

H. W. Foote (1938) has shown that the iodine adsorbed by the cuprous iodide is liberated and made available to the thiosulphate if a soluble thiocyanate is added to the solution just before the end point is reached in the usual titration. Under these conditions, the total iodine liberated is closely equivalent to the copper and the end point is sharp, the precipitate turning almost white. This simple modification permits the use of pure copper in the standardisation of thiosulphate solutions for general use. The **experimental procedure** is exactly as above. The thiosulphate solution is added until the yellow-brown colour due to iodine is nearly discharged, 2 ml. of starch solution is introduced, and titration is continued until near the end point. About 1·5 to 2·0 g. of A.R. ammonium thiocyanate is then added (to liberate the adsorbed iodine) and titration is continued until the blue colour is just discharged.

The principal reaction is :

$$2Cu^{++} + 4I^- \rightleftharpoons Cu_2I_2 + I_2.$$

It proceeds from left to right because of the insolubility of the cuprous iodide under the experimental conditions employed.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}06357 \text{ g. Cu.}$$

Note. J. J. Kolb (1939) has introduced the following modification which utilises perchloric acid for solution of the copper. The procedure has the advantage that all by-products are rapidly and completely removed by volatilisation (contrast the process for removing oxides of nitrogen described above) whilst cold dilute perchloric acid does not interfere in the titration.

Weigh out accurately 0·6 to 0·7 g. of pure copper into a small beaker provided with a clock-glass or Fisher " speedyvap " beaker cover, add 6 to 8 ml. of 60 to 70 per cent perchloric acid* and heat to boiling in a fume cupboard. Boil gently until solution is complete, continue the boiling for a few minutes, and cool slightly. Add an equal volume of distilled water, and boil for 2 minutes to eliminate any chlorine which may still be present. Cool to room temperature, transfer quantitatively to a 100 ml. volumetric flask, and make up to the mark. Mix well. To 25 ml. of this solution add 30 ml. of 10 per cent potassium iodide solution, allow to stand for 2 minutes, and titrate against the thiosulphate solution until the yellow colour is nearly discharged. Add 2 to 3 ml. of starch solution and titrate to near the end point. Add 1·5 to 2 g. of A.R. potassium or ammonium thiocyanate and continue the titration until the blue colour just disappears. The mixture at the end point is flesh-coloured.

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* See note as to danger attending the use of perchloric acid in Section **IV, 70.**

The results by this method are in close agreement with those obtained with potassium iodate.

F. With pure iodine. Pure iodine is prepared as described in Section **II, 12B** under Sublimation. This method has the advantage of giving a direct value, but suffers from the drawbacks that it is necessary to prepare pure dry iodine and the difficulty of weighing out accurately the volatile iodine. The weighing of the iodine is usually carried out in some form of weighing bottle containing a concentrated solution of potassium iodide ; the solution of iodine in potassium iodide has a lower vapour pressure, thus reducing the volatility.

Select two or three small weighing bottles fitted with well-ground stoppers and of such size that they will pass completely through the neck of a 350 or 500 ml. conical flask. Into one of these weigh out 2 to 2·5 g. of iodate-free potassium iodide and 0·5 ml. of water ; stopper the weighing bottle and weigh accurately. Remove the stopper, add 0·4 to 0·5 g. of pure iodine, quickly replace the stopper, and weigh again ; the difference between the two weighings gives the weight of iodine. Place the weighing bottle in the neck of the conical flask held in an inclined position and containing 200 ml. of water and about 1 g. of pure potassium iodide. Allow the bottle to slide to the bottom of the flask, but just as it falls remove the stopper and allow it to fall also. No iodine is thus lost. If the contents of the weighing bottle are washed into the water, a slight loss of iodine may occur. Titrate the solution, containing a known weight of iodine, with the sodium thiosulphate solution from a burette. When the liquid is pale yellow in colour, add 2 ml. of starch solution, and continue the titration dropwise until the blue colour is just destroyed. Repeat the determination with two other similar weighing bottles and 0·4 to 0·5 g. of iodine.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}12692 \text{ g. I.}$$

G. With a standard solution of iodine. If a solution of iodine which has been standardised against arsenious oxide (Section **III, 104A**) is available, this may be employed in the standardisation of a sodium thiosulphate solution. The procedure is identical with that given under **F** above.

Calculate the normality of the sodium thiosulphate solution as based upon that of the iodine solution (compare Section **III, 4A**).

III, 103. Preparation of 0·1*N* iodine solution.—*Discussion.* 0·335 Gram of iodine dissolves in 1 litre of water at 25°C. In addition to this small solubility, aqueous solutions of iodine have an appreciable vapour pressure of iodine, and therefore decrease slightly in concentration on account of volatilisation when handled. Both difficulties are overcome by dissolving the iodine in an aqueous solution of potassium iodide. Iodine dissolves readily in aqueous potassium iodide, the more concentrated the solution, the greater is the solubility of the iodine. The increased solubility is due to the formation of a tri-iodide ion :

$$I_2 + I^- \rightleftharpoons I_3^-.$$

The resultant solution has a much lower vapour pressure than a solution of iodine in pure water, consequently the loss by volatilisation is considerably diminished. Nevertheless the vapour pressure is still appreciable so that *precautions should always be taken to keep vessels containing iodine closed except during the actual titrations.* When an iodide solution of iodine is titrated with a reductant, the free iodine reacts with the reducing agent, this displaces the equilibrium to the left, and eventually all the tri-iodide is decomposed ; the solution therefore behaves as though it were a solution of free iodine.

Iodine solution attacks rubber, hence it should always be used with burettes fitted with glass taps. Since iodine and iodides are comparatively expensive, **all residual liquids or precipitates containing iodine in any form should be returned to the bottle marked "Iodine Residues."**

For the preparation of standard iodine solutions, A.R. or resublimed iodine and iodate-free (*e.g.* A.R.) potassium iodide should be employed. The solution may be standardised against pure arsenious oxide or against a sodium thiosulphate solution which has been recently standardised against potassium iodate, potassium bromate, or, less desirably, potassium permanganate or potassium dichromate. For work of the highest accuracy purposely-purified iodine may be weighed out directly, but in view of the volatility of the solid, this method is not recommended for beginners nor, indeed, is it necessary for most ordinary purposes. It is given here for the sake of completeness.

The equation :

$$I_2 + 2\epsilon \rightleftharpoons 2I^-$$

indicates that the equivalent weight is equal to the atomic weight, or 126·92.*

Procedure. **Preparation of 0·1*N* iodine.**

Method A. Dissolve 20 g. of iodate-free potassium iodide (*e.g.*, A.R.) in 30 to 40 ml. of water in a glass-stoppered 1 litre flask. Weigh out about 12·7 g. of A.R. or resublimed iodine on a watch glass on a rough balance (never on an analytical balance on account of the iodine vapour), and transfer it by means of a small dry funnel into the concentrated potassium iodide solution. Insert the glass stopper into the flask, and shake in the cold until all the iodine has dissolved. Allow the solution to acquire room temperature, and make up to the mark with distilled water.

The iodine solution is best preserved in small glass-stoppered bottles. These should be filled completely and kept in a cool dark place.

Method B. Purify resublimed or A.R. iodine as described in Section **II, 12B.** Secure a large weighing bottle provided with a well-fitting ground glass stopper. Place 20 g. of pure potassium iodide and 5 ml. of water into it ; the solid will dissolve completely on gentle shaking. When the bottle and contents have acquired room temperature, weigh them accurately to 0·1 mg. Weigh out 6·0 to 6·5 g. of the purified iodine on a rough balance and introduce it carefully without splashing into the weighing bottle. Allow to stand (say, for 20 minutes) in order to attain the room temperature ; and weigh again to the nearest 0·1 mg. Immediately after the weighing transfer the solution quantitatively to a glass-stoppered 500 ml. volumetric flask, and make up to the mark with distilled water. Stopper the flask, and store it in a dark place.

Calculate the normality of the iodine solution from the weight of pure iodine employed. A 0·1*N* solution contains 12·692 g. of iodine per litre.

III, 104. Standardisation of iodine solutions.†—

A. With arsenious oxide. *Discussion.* A.R. Arsenious oxide of 99·9 per cent purity can be obtained commercially ; the U.S. Bureau of Standards supply a product of 99·98 per

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* This also follows from the hypothetical equation :

$$I_2 + H_2O = 2HI + O.$$

† Prepared by *Method A*, Section **III, 103.**

cent guaranteed purity.* This substance therefore provides an excellent primary standard for the standardisation of iodine solutions. The reaction between arsenious oxide and iodine is a reversible one :

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-\dagger,$$

and proceeds quantitatively from left to right if the hydrogen iodide is removed from the solution as fast as it is formed. This may be done by the addition of sodium bicarbonate ; sodium carbonate and sodium hydroxide cannot be used since they react with the iodine forming iodide, hypoiodite and iodate. Actually it has been shown that the complete oxidation of the arsenite occurs when the pH of the solution lies between 4 and 9, the best value being 6·5, which is very close to the neutral point. Buffer solutions (Section **I, 20**) are employed to maintain the correct pH. A 0·12*N* solution of sodium bicarbonate saturated with carbon dioxide (carbonic acid) has a pH of 7 ; a solution saturated with both borax and boric acid has a pH of about 6·2, whilst a Na_2HPO_4–NaH_2PO_4 solution is almost neutral. Any of these three buffer solutions is suitable, but the first-named is generally employed as already stated.

Procedure. Weigh out accurately about 2·5 g. of finely powdered A.R. arsenious oxide (1), transfer to a 400 ml. beaker, and dissolve it in a concentrated solution of sodium hydroxide, prepared from 2 g. of iron-free sodium hydroxide (*e.g.*, A.R.) and 20 ml. of water. Dilute to about 200 ml., and neutralise the solution with *N* hydrochloric acid, using a strip of litmus paper as indicator. When the solution is faintly acid, remove the litmus paper by means of a stirring rod and carefully rinse both the rod and the paper. Transfer the contents of the beaker quantitatively to a 500 ml. volumetric flask, add 2 g. of pure sodium bicarbonate, and, when

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* Arsenious oxide of 99·95 per cent assay value is obtainable from the Mallinckrodt Chemical Works, U.S.A. (See Appendix, Sections **A, 8, 9.**) If there is any doubt as to the purity of the arsenious oxide, it may be purified by dissolving in hot dilute hydrochloric acid (1 : 2), filtering and cooling the filtrate. The supernatant liquor is poured off, the crystals washed with water, dried at 105° to 110°C for 1 to 2 hours, and then sublimed (Section **II, 12B**). The sublimate may be dried for 12 to 24 hours in a desiccator over concentrated sulphuric acid.

Pure arsenious oxide is not appreciably hygroscopic and, except for work of the highest accuracy, it is unnecessary to dry it before use.

† The reaction is sometimes written :

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI.$$

This equation shows that the equivalent weight of arsenious oxide in this reaction is 1/4 mol, or 197·82/4 = 49·46.

all the salt has dissolved, dilute to the mark. Shake well (2).

Measure out from a **burette** (this is advisable owing to the poisonous properties of the solution) 25 ml. of the arsenite solution into a 250 ml. conical flask (3), add 25 to 50 ml. of water, 5 g. of sodium bicarbonate and 2 ml. of starch solution. Swirl the solution carefully until the bicarbonate has dissolved. Then titrate slowly with the iodine solution, contained in a burette, to the first blue colour.

Alternatively, the arsenite solution may be placed in the burette, and titrated against 25 ml. of the iodine solution contained in a conical flask. When the solution has a pale yellow colour, add 2 ml. of starch solution, and continue the titration slowly until the blue colour is just destroyed.

For either method, further titrations should be carried out until individual titrations agree within 0·1 ml. Not more than 3 titrations should be necessary.

Calculate the normality of the iodine solution. A 0·1*N* solution of arsenious oxide contains 4·946 g. As_2O_3 per litre.

Notes. 1. If an exactly 0·1*N* solution is required, this is obtained by weighing out exactly 2·473 g. of arsenious oxide.

2. For the preparation of sodium arsenite solution with a Na_2HPO_4/NaH_2PO_4 buffer mixture, proceed as follows (Washburn, 1908). Weigh out accurately about 2·47 g. of pure dry arsenious oxide into a 500 ml. volumetric flask, dissolve it in a concentrated solution containing 6 g. of pure sodium hydroxide, add 5 ml. of pure syrupy phosphoric acid (0·15 mol.), and dilute to the mark. This solution will preserve its titration value indefinitely.

3. If it is desired to base the standardisation directly upon arsenious oxide without the intermediate use of a volumetric flask, proceed as follows. Weigh out accurately about 0·2 g. of pure arsenious oxide into a conical flask, dissolve it in 10 ml. of *N* sodium hydroxide, and add a small excess of dilute sulphuric acid (say, 12 to 15 ml. of *N* acid). Then add carefully a solution of 5 g. of sodium bicarbonate in 50 ml. of water, followed by 2 ml. of starch solution. Titrate slowly against the iodine solution to the first blue colour. Repeat with two other similar quantities of arsenious oxide.

Calculate the normality of the iodine solution.

B. With standard sodium thiosulphate solution. Sodium thiosulphate solution, which has been recently standardised, preferably against pure potassium iodate, is employed. Transfer 25 ml. of the iodine solution to a 250 ml. conical flask, dilute to 100 ml., and add the standard thiosulphate solution from a burette until the solution has a pale yellow colour. Add 2 ml. of starch solution, and continue the addition of the thiosulphate solution slowly until the solution is just colourless. Repeat the titration with two further 25 ml. portions of the iodine solution. The titrations should agree within 0·1 ml.

From the known normality of the sodium thiosulphate solution, calculate the normality of the iodine solution (compare Section **III, 4A**).

ANALYSES INVOLVING THE USE OF STANDARD SODIUM THIOSULPHATE SOLUTION, STANDARD IODINE SOLUTION, OR STANDARD SODIUM ARSENITE SOLUTION

III, 105. Determination of copper in crystallised copper sulphate.—For practice in this estimation, the student may determine the percentage of copper in A.R. copper sulphate, $CuSO_4.5H_2O$.

Method A. Weigh out accurately about 3·0 g. of the salt, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 50 ml. of this solution into a 250 ml. conical flask, add 3 g. of potassium iodide (or 30 ml. of a 10 per cent solution) (1), and titrate the liberated iodine with standard 0·1*N* sodium thiosulphate (Section **III, 102**, *Procedure E*) (2). Repeat the titration with two other 50 ml. portions of the copper sulphate solution.

The reaction is :

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4,$$

from which it follows that :

$$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3,$$

or $$1 \text{ ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}06357 \text{ g. Cu.}$$

Calculate the percentage of copper in crystallised copper sulphate.

Notes. 1. If in a similar determination, free mineral acid is present, a few drops of dilute sodium carbonate solution must be added until a *faint* permanent precipitate remains, and this is removed by means of a drop or two of acetic acid. The potassium iodide is then added and the titration continued. For accurate results, the solution should have a *p*H of 4 to 5·5.

2. If difficulty is experienced in determining the end point, a large excess (7 to 8 g.) of potassium iodide may be added ; this largely dissolves the precipitated cuprous iodide with the formation of a complex salt. This modification is expensive. A simpler

method is to add 2 g. of ammonium thiocyanate towards the end of the titration, *viz.*, just after the blue starch colour diminishes in intensity.

Method B. Discussion. The following method, due to G. Bruhns (1918), replaces part of the expensive potassium iodide by the cheaper potassium thiocyanate. It is based upon the fact that cuprous thiocyanate is *less* soluble than cuprous iodide leading to the following reaction in aqueous solution :

$$Cu_2I_2 + 2KCNS = Cu_2(CNS)_2 + 2KI \quad \text{(i)},$$

and also upon the following reactions :

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4 \quad \text{(ii)};$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6 \quad \text{(iii)};$$
$$2CuSO_4 + 4KCNS = 2Cu(CNS)_2 + 2K_2SO_4 \quad \text{(iv)};$$
$$2Cu(CNS)_2 + 2Na_2S_2O_3 = Cu_2(CNS)_2 + 2NaCNS + Na_2S_4O_6 \quad \text{(v)}.$$

Bruhns uses two alternative procedures for the titration of a solution of a copper salt slightly acidified with sulphuric acid. In the first he employs a solution containing 24·8 g. crystallised sodium thiosulphate and 25 to 30 g. of potassium thiocyanate per litre, and titrates this with the copper solution in the presence of a little starch as indicator. In the second procedure he employs a solution containing 24·8 g. of crystallised sodium thiosulphate, 25 g. of potassium thiocyanate and 8 g. of potassium iodide per litre, and uses this directly in the titration of the copper solution in the presence of starch. Only mercury and silver, which form insoluble iodides, interfere ; the influence of ferric salts is prevented by the addition of oxalic acid or of a soluble fluoride.

For many purposes it is sufficient to add a little potassium iodide to the solution, followed by excess of potassium thiocyanate ; the solution is then titrated against standard thiosulphate in the usual way.

Procedure. Prepare the copper sulphate solution as in *Method A*. Pipette 50 ml. of the solution into a conical flask, add 3 to 5 ml. of 10 per cent potassium iodide solution followed by about 2 g. of potassium thiocyanate. Titrate immediately against standard 0·1*N* sodium thiosulphate ; towards the end of the titration dilute with about 100 ml. of water and add 2 ml. of starch indicator.

Calculate the percentage of copper in crystallised copper sulphate.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}06357 \text{ g. Cu.}$$

III, 106. Determination of copper in an ore.—*Discussion.* Of the common elements which are usually associated with copper ores, those that interfere with the iodometric estimation are iron, arsenic and antimony. Ferric iron is reduced by iodide :

$$2Fe^{+++} + 2I^{-} \rightleftharpoons 2Fe^{++} + I_2,$$

but by the addition of excess of fluoride, the ferric iron is converted into the complex $[FeF_6]^{---}$, which yields so small a concentration of ferric ions that it has no oxidising action upon the iodide. Arsenic and antimony in the trivalent form react with iodine, but in consequence of the oxidising medium usually employed to bring the sample into solution they will be present in the quinquevalent form. Arsenic and antimonic compounds will not oxidise iodide in a solution having a *p*H greater than about 3·2. By the use of excess of ammonium bi-fluoride, NH_4HF_2, which acts as a buffer, the *p*H of the solution can be maintained above 3·2 ; under these conditions the reduction of the cupric ion proceeds to completion. The concentration of the fluoride should be 1·0 to 1·6 molar.

Procedure. Weigh out accurately 0·5 to 1·0 g. of the finely powdered copper ore* into a 250 ml. beaker, add 10 to 15 ml. of concentrated nitric acid, and heat until the ore is well disintegrated and all the copper is in solution. Evaporate to a volume of 5 ml. (*e.g.*, on an electric hot plate). Add 10 ml. of concentrated hydrochloric acid and 10 ml. of 1 : 1 sulphuric acid, and evaporate to dense white fumes. To complete the oxidation of arsenic, etc., add cautiously 20 ml. of water and 10 ml. of saturated bromine water, and boil the solution until all the bromine is expelled. Filter off the residue on a small quantitative filter paper (1), and collect the filtrate in a 250 ml. conical flask. Wash the residue with hot 1 per cent nitric acid until the washings are colourless. Concentrate the filtrate to about 30 ml. (place a short funnel in the neck of the flask), add 0·5 g. of urea to the hot solution, and heat to boiling for 1 minute ; this removes any nitrous acid or oxides of nitrogen which may be present. To the cold solution add ammonia solution (1 : 1) dropwise until the solution smells slightly of ammonia. This will precipitate all the iron as hydroxide ; an excess of ammonia solution should be avoided. Add 2·0 g. of ammonium bi-fluoride NH_4HF_2 (2) and shake until all the ferric hydroxide has dissolved. Now add 3 g. of A.R. potassium iodide dissolved in 5 to 10 ml. of water, and titrate at once with standard 0·1*N* sodium thiosulphate, which has been standardised against pure copper (Section **III, 102,** *Procedure F*), adding 2 ml. of starch solution near the end point. The colour change is from blue to yellowish-white; the blue colour should not return within 10 to 15 minutes (3). Repeat the determination with another sample of the ore.

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* Ridsdale's " Copper pyrites, No. 26 " (one of the Analysed Samples for Students) is suitable.

Calculate the percentage of copper in the copper ore.

Notes. 1. If the residue is small in amount or light coloured, the filtration may be omitted. The subsequent washing with 1 per cent nitric acid and treatment with urea is then unnecessary.

2. About 1 g. of ammonium bi-fluoride should be added for each 0·1 g. of iron present.

3. If Foote's thiocyanate method (Section **III, 102E**) is employed, the colour change is more or less permanent.

III, 107. Determination of manganese dioxide in pyrolusite. —*Discussion.* All higher oxides of the heavy metals which evolve chlorine upon treatment with concentrated hydrochloric acid may be determined with accuracy by passing the chlorine into excess of potassium iodide solution, and titrating the liberated iodine with standard sodium thiosulphate or sodium arsenite solution. It is essential to be certain that all the chlorine reacts with the potassium iodide solution. With pyrolusite, the following reactions occur:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2;$$
$$2KI + Cl_2 = 2KCl + I_2.$$

Procedure. A distillation apparatus, such as is portrayed diagrammatically in Fig. 3-8 or Fig. 3-9, is employed. The apparatus fitted with ground glass joints is to be preferred owing to the attack of chlorine upon rubber.

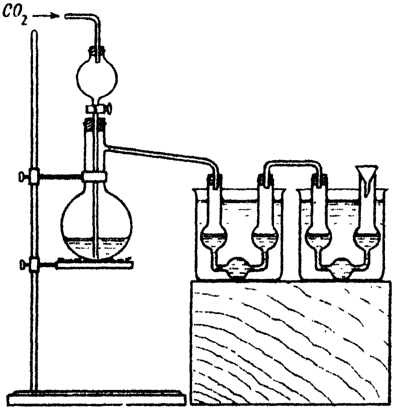

FIG. 3-8.

/ The apparatus in Fig. 3-8 consists of a distillation flask of about 200 ml. capacity, connected to two U (Péligot) tubes containing potassium iodide solution. In Fig. 3-9 a 250 to 300 ml. flask is provided with two ground glass joints at **A** and **B**; the tube from **B** passes into a small conical flask containing potassium iodide solution; **C** is a small tube containing glass beads moistened with potassium iodide solution; the rest of the apparatus is self-explanatory. Weigh out accurately about 0·2 g. of the finely powdered mineral* into a small weighing tube (1 cm. wide and 2 cm. long is a convenient size), and introduce the tube and contents into the distillation flask; connect up the apparatus as shown in the Figure. Introduce 100 ml. of water containing 3·5 g. of iodate-free (*e.g.*, A.R.) potassium iodide into the absorption apparatus, which should be immersed in cold water. Place 25 ml. of concentrated hydrochloric acid into the separating funnel, and add it to the contents of the flask; meanwhile maintain a *very slow* stream of carbon dioxide through the apparatus. Heat the mixture very gently so that chlorine is slowly evolved. Increase the temperature *gradually* to the boiling point, and finally pass a slow current of carbon dioxide through the boiling solution until all the chlorine has been expelled (about 15 minutes). Immediately before the heating is stopped, increase the current of carbon dioxide in order to prevent the solution in the absorption vessels from passing back into the flask. Disconnect the absorption vessels. With the apparatus of Fig. 3-8, the contents of the U-tubes are quantitatively transferred to a conical flask; with the apparatus of Fig. 3-9, the tubes and beads are well rinsed with water and removed from the flask. Titrate the liberated iodine at once with standard 0·1*N* sodium thiosulphate in the usual manner. If desired, the solution may be made up to 100 ml. in a volumetric flask, and 50 ml. portions titrated against the sodium thiosulphate solution; if this procedure is adopted, the weight of the mineral may be increased to 0·3 to 0·4 g.

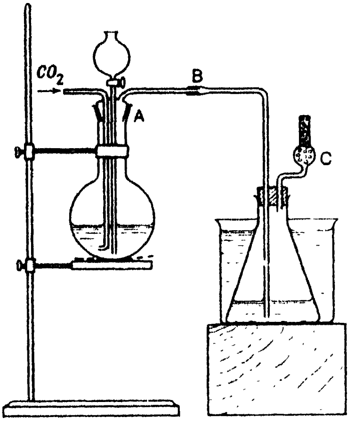

FIG. 3-9.

Calculate the percentage of MnO_2 in the mineral.

$$1 \text{ Ml. } N \ Na_2S_2O_3 \equiv 0{\cdot}04347 \text{ g. } MnO_2.$$

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* Ridsdale's "Pyrolusite (Mn) Ore, No. 18" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Manganese Ore 'A'" (one of the British Chemical Standards) is suitable.

Note. Red lead Pb_3O_4 and lead dioxide PbO_2 may be estimated in a similar manner (compare Section **III, 57,** *Note*).

III, 108. Determination of chlorates and of bromates.—*Discussion.* Chlorates and bromates may be estimated by the distillation process described in the previous Section for pyrolusite. The process of distillation may be avoided in these and similar cases* by mere digestion with hydrochloric acid and potassium iodide solution at an elevated temperature ; decomposition is quantitative.

$$KClO_3 + 6HCl = KCl + 3Cl_2 + 3H_2O ;$$

$$3Cl_2 + 6KI = 6KCl + 3I_2.$$

$$Na_2S_2O_3 \equiv I \equiv KClO_3/6 \equiv KBrO_3/6.$$

A strong bottle (" pressure bottle ") with a very accurately ground stopper is necessary. Generally, the ordinary stoppered bottle of commerce is not sufficiently tight, and it is better to regrind the stopper with a little *very fine* emery and water. It must then be tested by securing the stopper tightly and immersing in hot water ; if any bubbles of air pass through the stopper, the bottle is useless. The stopper may be secured by means of fine copper wire threaded through a piece of rubber tubing securely fixed to the neck of the bottle, or by means of a special screw clamp (Fig. 3-10).†

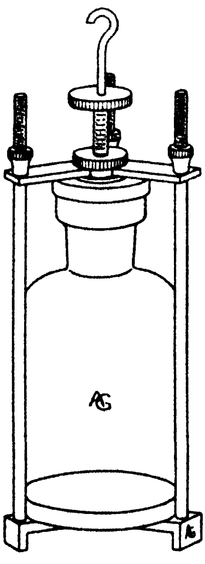

FIG. 3-10.

For practice, the student may determine the percentage of ClO_3 (or of BrO_3) in potassium chlorate (or potassium bromate), preferably of A.R. quality.

Procedure. Weigh out accurately 0·25 to 0·30 g. of the finely-powdered

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* For example, chromates and dichromates. These yield the green chromic chloride and an equivalent quantity of iodine :

$$2K_2CrO_4 + 6KI + 16HCl = 10KCl + 2CrCl_3 + 3I_2 + 8H_2O ;$$

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 3I_2 + 7H_2O.$$

Here it is necessary to dilute the solution very considerably in order to prevent the green colour of the chromic salt from masking the blue colour of the starch in the subsequent titration with standard sodium thiosulphate solution.

$$1\ \text{Ml.}\ N\ Na_2S_2O_3 \equiv 0{\cdot}06474\ \text{g.}\ K_2CrO_4 \equiv 0{\cdot}04904\ \text{g.}\ K_2Cr_2O_7.$$

† Such bottles may be purchased, for example, from A. Gallenkamp and Co. Ltd., London, E.C.2, England, or from the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.

potassium chlorate into a pressure bottle, add 7 g. of iodate-free potassium iodide dissolved in a *small* volume of water, and displace the air from the bottle by means of carbon dioxide from a Kipp's apparatus or from a cylinder. Add 25 ml. of concentrated hydrochloric acid, insert the stopper, fasten it down securely, and wrap the bottle in a thick duster. Immerse the whole in cold water in a water bath, heat the water gradually to boiling, and continue the boiling for 1 hour. Allow the water to cool, and when quite cold, remove the bottle, open it, transfer the contents quantitatively into a 250 ml. volumetric flask, and make up to the mark. Shake well. Titrate 50 ml. portions with standard $0{\cdot}1N$ sodium thiosulphate, using starch as indicator.

Calculate the percentage of ClO_3 in the sample of potassium chlorate.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}11391 \text{ g. } ClO_3 \equiv 0{\cdot}02043 \text{ g. } KClO_3.$$

III, 109. Volumetric determination of lead.—*Discussion.* The lead is precipitated as the chromate with potassium chromate or dichromate solution in a medium buffered with a mixture of acetic acid and sodium or ammonium acetate. The precipitate is washed with water, dissolved in dilute hydrochloric acid, treated with potassium iodide solution, and the liberated iodine titrated with a standard solution of sodium thiosulphate.

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 = PbCrO_4 + 2K.C_2H_3O_2\,;$$
$$PbCrO_4 + 2HCl = H_2CrO_4 + PbCl_2\,;$$
$$2H_2CrO_4 + 6KI + 12HCl = 2CrCl_3 + 6KCl + 3I_2 + 8H_2O.$$

Thus $Pb \equiv 3I$, or 1 ml. $N\ I \equiv 1$ ml. $N\ Na_2S_2O_3 \equiv 0{\cdot}06907$ g. Pb.

Another method, which is sometimes used, consists in adding excess of $0{\cdot}1N$ potassium dichromate to the solution buffered with alkali acetate, boiling for 2 to 3 minutes, filtering the precipitate on a sintered Jena glass crucible, washing the precipitate well with cold water, and determining the excess of dichromate in the cooled filtrate either iodometrically by the addition of excess of potassium iodide and titration with standard thiosulphate solution, or with standard ferrous ammonium sulphate solution.

For practice, the student may determine the percentage of lead in lead nitrate, preferably of A.R. purity.

Procedure. Weigh out accurately about 0·3 g. of A.R. lead nitrate, dissolve it in excess of dilute acetic acid (1 : 4), and add 2 g. of sodium acetate* ; dilute to 150 ml. Heat the solution to boiling, and add from a pipette 10 ml. of hot 4 per cent potassium chromate solution. Boil gently for 5 to 10 minutes, filter the lead chromate through a sintered glass crucible, and wash several times with dilute sodium acetate solution. Transfer the precipitate quantitatively to a 250 ml. conical flask, dissolve it in dilute hydrochloric acid (1 : 1), add 20 ml. of 10 per cent potassium iodide solution and stir gently. Titrate at once with standard 0·1*N* sodium thiosulphate until the iodine colour has nearly disappeared, add 2 ml. of starch solution, and continue the titration until the colour of the solution changes to a clear green. Dilution facilitates the detection of the end point.

Calculate the percentage of lead in the sample of lead nitrate.

III, 110. Analysis of hydrogen peroxide.—*Discussion.* Hydrogen peroxide reacts with iodide in acid solution in accordance with the equation :

$$H_2O_2 + 2H^+ + 2I^- = I_2 + 2H_2O.$$

The reaction velocity is comparatively slow, but increases with increasing concentration of acid. The addition of 3 drops of a neutral 20 per cent ammonium molybdate solution renders the reaction almost instantaneous, but as it also accelerates the atmospheric oxidation of the hydriodic acid, the titration is best conducted in an atmosphere of carbon dioxide.

The iodometric method has the advantage over the permanganate method (Section **III, 55**) that it is less affected by stabilisers which are sometimes added to commercial hydrogen peroxide solutions. These preservatives are often boric acid, salicylic acid and glycerol, and render the results obtained by the permanganate procedure less accurate.

Procedure. Dilute the hydrogen peroxide solution to 2-volume strength (*ca.* 0·6 per cent H_2O_2). Thus, if a " 10-volume " hydrogen peroxide is used, transfer 20 ml. by means of a burette or pipette to a 100 ml. volumetric flask, and make up to the mark. Shake well. Remove 10 ml. of this diluted solution, and add it gradually and with constant stirring to a solution of 2 g. of pure potassium iodide in 200 ml.

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* The addition of alkali acetate is only essential when potassium dichromate (*e.g.*, 10 ml. of the saturated solution) is used for precipitation.

of $2N$ sulphuric acid (1 : 20) contained in a stoppered bottle. Allow the mixture to stand for 15 minutes, and titrate the liberated iodine with standard $0{\cdot}1N$ sodium thiosulphate, adding 2 ml. of starch solution when the colour of the iodine has been nearly discharged. Run a blank determination at the same time.

Better results are obtained by transferring 10 ml. of the diluted hydrogen peroxide solution to a conical flask, and adding 180 ml. of $2N$ (1 : 20) sulphuric acid. Pass a slow stream of carbon dioxide through the flask, add 20 ml. of 10 per cent potassium iodide solution, followed by 3 drops of 20 per cent ammonium molybdate solution. Titrate the liberated iodine immediately with standard $0{\cdot}1N$ sodium thiosulphate in the usual way.

Repeat the titration with two other 10 ml. portions of the peroxide solution.

Calculate the weight of H_2O_2 in 1000 ml. of the original solution.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}01701 \text{ g. } H_2O_2.$$

Note. The above method is available for all per-salts.

III, 111. Determination of the available chlorine in bleaching powder.—*Discussion.* Bleaching powder consists essentially of a mixture of calcium hypochlorite $Ca(OCl)_2$ and the basic chloride $CaCl_2,Ca(OH)_2,H_2O$; some free slaked lime is usually present. The active constituent is the hypochlorite, which is responsible for the bleaching action. Upon treating bleaching powder with acid, chlorine is liberated :

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2Cl_2 + 2H_2O.$$

The **available chlorine** refers to the chlorine liberated by the action of dilute acids, and is expressed as the percentage by weight of the bleaching powder. The bleaching powder of commerce contains 36 to 38 per cent of available chlorine.

Two methods are in common use for the determination of the available chlorine. In the first, the bleaching-powder solution or suspension is treated with an excess of a solution of potassium iodide, and strongly acidified with acetic acid :

$$Ca(OCl)_2 + 4KI + 4H.C_2H_3O_2$$
$$= CaCl_2 + 4K.C_2H_3O_2 + 2I_2 + 2H_2O.$$

The liberated iodine is titrated with standard sodium thiosulphate solution. The solution should not be acidified with hydrochloric acid, for the little calcium chlorate which is usually present, by virtue of the decomposition of the hypochlorite, will react slowly with the potassium iodide and liberate iodine :

$$HClO_3 + 6KI + 5HCl = 6KCl + 3I_2 + 3H_2O.$$

In the second method, the bleaching powder solution or suspension is titrated against standard 0·1*N* sodium arsenite. No internal indicator is at present available for the detection of the end point, since hypochlorite destroys most organic dyes. An external indicator, potassium iodide-starch paper, is employed. As long as excess of hypochlorite is present, a drop of the solution being titrated will turn iodide-starch paper blue ; at the end point, a drop of the solution will no longer produce a blue stain. The external indicator may be dispensed with by adding excess of the standard arsenite solution, and titrating back with standard iodine solution, using starch as indicator.

$$Ca(OCl)_2 + As_2O_3 = CaCl_2 + As_2O_5.$$

The **potassium iodide-starch paper** may be purchased, or it can be prepared as follows. Boil 1 g. of starch with 100 ml. of water, filter the solution, and add 0·1 to 0·2 g. of pure potassium iodide to the filtrate. Dip strips of filter paper into the solution, and dry them on a porcelain or glass plate at 40° to 50°C.

Procedure A (**iodometric method**). Weigh out accurately about 5 g. of the bleaching powder into a clean glass mortar. Add a little water, and rub the mixture to a smooth paste. Add a little more water, triturate with the pestle, allow the mixture to settle, and pour off the milky liquid into a 500 ml. volumetric flask. Grind the residue with a little more water, and repeat the operation until the whole of the sample has been transferred to the flask either in solution or in a state of very fine suspension, and the mortar washed quite clean. The flask is then filled to the mark with distilled water, well shaken, and 50 ml. of the turbid liquid immediately withdrawn with a pipette. This is transferred to a 250 ml. conical flask, 25 ml. of water added, followed by 2 g. of iodate-free potassium iodide (or 20 ml. of a 10 per cent solution) and 10 ml. of glacial acetic acid. Titrate the liberated iodine with standard 0·1*N* sodium thiosulphate ; add 2 ml. of starch solution when the solution has a pale yellow colour, and continue the titration dropwise until the blue colour just disappears. Repeat the determination with two other 50 ml. portions of the well-mixed suspension.

Calculate the available chlorine in the bleaching powder.

$$1\ \text{Ml.}\ N\ Na_2S_2O_3 \equiv 0{\cdot}03546\ \text{g. Cl.}$$

Procedure B (**arsenite method**). Prepare a bleaching powder solution or suspension as is described in *Procedure A*. Transfer 50 ml. of the well-mixed suspension to a 250 ml. beaker, and titrate with the standard $0{\cdot}1N$ sodium arsenite (Section **III, 104A**), delivered from a burette, until a drop of the mixture removed with a glass rod and brought into contact with potassium iodide-starch paper gives no blue stain. The first titration will be approximate. In subsequent titrations, add the arsenite solution until within 1 ml. of the previously determined end point, and remove test drops only during the completion of the titration.

The use of the external indicator may be avoided by adding excess (say, 75 ml.) of the standard sodium arsenite solution, and titrating back the excess with standard $0{\cdot}1N$ iodine, using starch as indicator.

Calculate the percentage of available chlorine in the sample of bleaching powder.

$$1 \text{ Ml. } N\ As_2O_3 \equiv 0{\cdot}03546 \text{ g. Cl.}$$

III, 112. Determination of hypochlorites.—This problem arises in the analysis of sodium hypochlorite solution and of " high test hypochlorite " (H.T.H.). The latter substance, marketed in America, consists of calcium hypochlorite of 75 to 100 per cent purity ; it is more stable than ordinary bleaching powder, keeps well, is almost non-hygroscopic, and gives a practically clear aqueous solution.

Both the iodometric and sodium arsenite methods described in the previous Section may be used, and need therefore not be repeated here.

III, 113. Determination of antimony.—*Discussion.* Antimonious oxide reacts with iodine in a similar way to arsenious oxide (Section **III, 104**), and the antimony may be determined by titration with a standard solution of iodine :

$$Sb_2O_3 + 2I_2 + 2H_2O \rightleftharpoons Sb_2O_5 + 4HI.$$

The hydriodic acid must be removed as formed by the addition of excess of sodium bicarbonate solution. To prevent the precipitation of antimonious hydroxide when an acid solution is diluted or neutralised, some tartrate is added, which forms a soluble complex salt, for example :

$$SbCl_3 + KH.C_4H_4O_6 + 3NaHCO_3$$
$$= K(SbO)C_4H_4O_6 + 3NaCl + 2H_2O + 3CO_2 ;$$
$$K(SbO)C_4H_4O_6 + I_2 + 4NaHCO_3$$
$$= KNa.C_4H_4O_6 + Na_2HSbO_4 + 2NaI + H_2O + 4CO_2.$$

This method is satisfactory for tartar emetic, antimony oxide, and certain other antimony compounds, but fails when applied to alloys in which antimony is not the principal constituent (5 to 20 per cent antimony). The potassium bromate method (Sections **III, 135, 137**) or the permanganate method (Section **III, 117**) may then be used, and is, in general, more satisfactory for the volumetric estimation of antimony.

For practice, the student may determine the percentage of antimony in tartar emetic $K(SbO)C_4H_4O_6,0{\cdot}5H_2O$ or in the anhydrous A.R. potassium antimonyl tartrate.

Procedure (**antimony in tartar emetic**). Weigh out accurately about 2 g. of the finely-powdered A.R. tartar emetic (or 2·5 g. of the hydrated compound), dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake well. Transfer 50 ml of the solution to a 250 ml. conical flask by means of a **burette (a pipette should NOT be used, for antimony salts are nearly as poisonous as those of arsenic)**, add 20 ml. of a cold saturated solution of pure sodium bicarbonate (about 10 ml. are required to about 0·1 g. of Sb_2O_3) and 2 ml. of starch solution. Titrate with standard 0·1*N* iodine until the blue colour just appears. The titration must be carried out immediately after the sodium bicarbonate solution is added, otherwise a portion of the metal is precipitated as antimonious hydroxide, which reacts extremely slowly with the iodine. Repeat the determination with two other 50 ml. volumes of the solution.

Calculate the percentage of antimony in the sample used.

$$1 \text{ Ml. } N \text{ I} \equiv 0{\cdot}06088 \text{ g. Sb.}$$

III, 114. Determination of antimony in antimonic oxide and in antimonates.—Here the reaction is the reverse of that for the determination of antimonious compounds :

$$Sb_2O_5 + 4H^+ + 4I^- \rightleftharpoons Sb_2O_3 + 2I_2 + 2H_2O.$$

The antimonic oxide or antimonate is treated with concentrated hydrochloric acid and an at least five-fold excess of potassium iodide in an apparatus similar to that used in Section **III, 107**, and the iodine liberated is collected in potassium iodide solution. The free iodine in the distillate is then titrated with a standard solution of 0·1*N* sodium thiosulphate.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 1 \text{ ml. I} \equiv 0{\cdot}08088 \text{ g. } Sb_2O_5.$$

III, 115. Determination of arsenic in arsenic oxide and in arsenates.—The reaction is the reverse of that employed in the standardisation of iodine with sodium arsenite solution (Section **III, 104A**) :

$$As_2O_5 + 4H^+ + 4I^- \rightleftharpoons As_2O_3 + 2I_2 + 2H_2O.$$

For the estimation of arsenic in arsenic pentoxide or in, say, commercial lead arsenate, shake an amount of the material equivalent to about 0·15 g. As_2O_3 (*e.g.*, 0·5 g. of lead arsenate) in a glass-stoppered bottle with 30 ml. of concentrated hydrochloric acid, add 0·5 g. of potassium iodide, and after 15 minutes titrate the liberated iodine with standard 0·1*N* sodium thiosulphate, using starch as indicator. It is desirable, and for very small quantities of arsenates it is essential, to work in an atmosphere of carbon dioxide in order to avoid the liberation of iodine by exposure to the air. A "blank" should be run simultaneously with the iodide and acid under the same conditions, and the resulting thiosulphate titre deducted as a correction.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 1 \text{ ml. } N\ I \equiv 0{\cdot}05746 \text{ g. } As_2O_5.$$

Note. For those arsenates which do not yield an insoluble salt with sulphuric acid, 12*N* sulphuric acid gives good results.

III, 116. Determination of tin.—*Discussion.* The method depends upon the oxidation of stannous chloride to stannic chloride by means of iodine solution in the presence of concentrated hydrochloric acid :

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

A small amount of sulphuric acid is not objectionable, but nitric acid must be absent. Very few substances, particularly arsenic and antimony, ordinarily met with in analysis for tin interfere : foreign substances must not be present in such concentrations that they affect the action of the starch indicator. The determination must, however, be conducted in a non-oxidising atmosphere ; this is achieved by maintaining an atmosphere of carbon dioxide from a Kipp's apparatus or from a cylinder.

If the tin is present in the stannic state, it must be reduced by warming with pure (*e.g.*, A.R.) antimony (powdered), iron, lead, aluminium or nickel. When nickel is employed in the reduction, a large excess of hydrochloric acid must be present in order to prevent the precipitation of antimony which may be required in some analyses, for example, in type metal.

Attention is directed to the fact that it has been shown (F. L. Okell and J. Lumsden, 1935) that the iodimetric titration of stannous tin is subject to a variable error due to the presence of dissolved oxygen in the iodine solution. The error may be as high as 1 per cent for $0{\cdot}1N$ iodine and 10 per cent for $0{\cdot}01N$ iodine. It is accordingly recommended that for the determinations of tin described below the iodine solution be prepared in a carbon dioxide atmosphere with boiled-out distilled water which has been allowed to cool in carbon dioxide. The solution should be stored in the self-filling apparatus shown in Fig. 2-25 or Fig. 2-26 under carbon dioxide, the air in the burette and storage bottle being of course first displaced by carbon dioxide. It is found that iodine does not appreciably attack red rubber "pressure-tubing," but black lightly vulcanised tubing is unsatisfactory.

For practice, the student may estimate the tin in, and hence the purity of, A.R. stannous chloride $SnCl_2,2H_2O$, and also the tin in an alloy.

Procedure A (**tin in stannous chloride**). Weigh out accurately about 2 g. of A.R. stannous chloride, dissolve it in 150 ml. of concentrated hydrochloric acid, transfer to a 250 ml. volumetric flask, and make up to the mark with air-free distilled water. No appreciable oxidation of the tin occurs in this process. Transfer 50 ml. of the solution to a 250 ml. conical flask, dilute with 50 ml. of air-free water, and add 2 ml. of starch solution. Pass a current of carbon dioxide over the surface of the liquid, and titrate with standard $0{\cdot}1N$ iodine to the first appearance of a blue colour. Repeat the titration with two other 50 ml. portions of the solution.

Calculate the percentage of tin in the salt used, and therefrom its $SnCl_2,2H_2O$ content.

$$1 \text{ Ml. } N \text{ I} \equiv 0{\cdot}05935 \text{ g. Sn.}$$

Procedure B (**tin in an alloy**). Dissolve 0·2 to 2·0 g., accurately weighed, of the finely-divided alloy,* according to the percentage of tin present, in concentrated hydrochloric acid, transfer the solution quantitatively to a 350 ml. or 500 ml. wide-mouthed conical flask, add 50 ml. of concentrated hydrochloric acid, and dilute the solution to 200 ml. Add about 1 g. of finely-powdered pure antimony, *e.g.*, A.R. ($3SnCl_4 + 2Sb = 3SnCl_2 + 2SbCl_3$) or 1 g. of A.R. iron wire

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* Ridsdale's "White Metal, No. 8b" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "White Metal 'B'" is suitable. About 0·2 g. should be used.

($SnCl_4 + Fe = FeCl_2 + SnCl_2$) or 1 g. of aluminium turnings ($3SnCl_4 + 2Al = 3SnCl_2 + 2AlCl_3$). Insert a three-hole rubber stopper, carrying in one hole a gas inlet tube extending to the bottom of the flask, in the second hole a vertical condenser tube 15 to 20 cm. in length, and in the third a small stopper. Pass a slow stream of carbon dioxide through the flask, gradually heat to boiling, and continue the gentle ebullition for 30 minutes. Cool (preferably in ice) to about 10°C whilst a more rapid stream of carbon dioxide is passed through. When the solution is cold, continue the current of the gas, remove the stopper in the third hole, add 2 ml. of starch solution from a pipette, and insert the tip of a burette containing standard $0{\cdot}1N$ iodine. Titrate to the first permanent blue colour.

The iodine solution may be standardised against arsenious oxide or, better, against A.R. tin which has been dissolved and treated as in the above method.

Calculate the percentage of tin in the alloy.

III, 117. Determination of antimony and tin in type metal.—*Discussion.* The method given below combines the excellent permanganate method for the determination of antimony:

$$4MnO_4^- + 5Sb_2O_3 + 12H^+ = 4Mn^{++} + 5Sb_2O_5 + 6H_2O$$

or

$$Sb_2O_3 + 2O = Sb_2O_5,$$

and the iodimetric method for tin given in the previous Section.

Procedure. **Determination of antimony.** Weigh out accurately 1 g. of the finely-divided alloy* (or an amount corresponding to approximately 0·1 g. of antimony), dissolve it in 20 to 50 ml. of concentrated sulphuric acid (according to the amount of lead present), allow to cool, dilute *very carefully* to 100 ml., and allow to stand. Decant the clear liquid from the lead sulphate formed into a wide-mouthed 350 or 500 ml. conical flask, and boil for 5 minutes to expel sulphur dioxide. Boil the lead sulphate with the appropriate volume of concentrated hydrochloric acid†* and an equal volume of water. When the lead sulphate is completely in solution, wash back quantitatively into the main antimony solution, disregarding

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* The Bureau of Analysed Samples "White Metal 'A'" (one of the British Chemical Standards) is suitable for this estimation. About 1 g. should be used.

† Conc. H_2SO_4, ml.	0	10	20	30
Conc. HCl, ml.	30–50	30–35	15–20	10–15 (W. Pugh, 1933).

These volumes apply to a final volume of 200 ml.

any lead salt which may now be reprecipitated. Titrate the solution at 40° to 60°C with standard $0{\cdot}1N$ potassium permanganate, added slowly to prevent loss of chlorine, and when the end point has almost been reached add a few drops of methyl orange, and continue the titration until the colour of the indicator is discharged (compare Section **III, 135**).

The potassium permanganate solution may be standardised against arsenious oxide or sodium oxalate in the usual way. It is better, however, to use finely-powdered A.R. antimony* or anhydrous A.R. potassium antimonyl tartrate. The standard antimony solution may be prepared by dissolving about 3·0 g. of pure antimony, accurately weighed, in 30 ml. of concentrated sulphuric acid, diluting it, boiling off traces of sulphur dioxide, and making up to 500 ml. in a volumetric flask with 125 ml. of concentrated hydrochloric acid and water.

In the analysis of lead-tin alloys, the ratio of hydrochloric to sulphuric acid is important for the attainment of correct results ; too little hydrochloric acid leads to the precipitation of a basic antimony salt, whilst too much may cause reduction of the permanganate by chloride ions, with the liberation of chlorine, and the end point becomes barely perceptible.

Determination of tin. After the titration of the antimony by the permanganate solution is complete, add sufficient concentrated hydrochloric acid to bring this to 20 per cent by volume of the entire solution, and add 1 g. of finely-powdered pure antimony or 1 g. of A.R. iron wire. Insert a three-holed rubber stopper, and proceed exactly as described for the determination of tin in Section **III, 116B.**

Calculate the percentages of antimony and of tin in the alloy.

III, 118. Determination of sulphurous acid and of sulphites.—*Discussion.* The iodimetric estimation is based upon the equation :

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$

For accurate results, the following experimental conditions must be observed :

(i) the solutions shall be very dilute ;

(ii) the sulphite must be added slowly and with constant stirring to the iodine solution, and not conversely ; and

(iii) exposure of the sulphite to the air be minimised.

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* A.R. antimony can be obtained from the Mallinckrodt Chemical Works, U.S.A. See Appendix, Section **A, 9.**

Under these conditions the following possible errors are almost entirely avoided :

(*a*) loss of sulphur dioxide by volatilisation ;

(*b*) precipitation of sulphur by the " total " reaction

$$3H_2SO_3 = 2H_2SO_4 + S + H_2O,$$

which is catalysed by hydriodic acid, and also by the reaction

$$H_2SO_3 + 4HI = 2I_2 + S + 3H_2O \text{ ; and}$$

(*c*) oxidation of sulphite to sulphate.

In determinations of sulphurous acid and sulphites, excess of standard $0{\cdot}1N$ iodine is diluted with several volumes of water, acidified with hydrochloric or sulphuric acid, and a known volume of the sulphite or sulphurous acid solution is added slowly and with constant stirring from a burette, with the jet close to the surface of the liquid. The excess of iodine is then titrated with standard $0{\cdot}1N$ sodium thiosulphate. Solid soluble sulphites are finely powdered and added directly to the excess of the iodine solution. Insoluble sulphites (*e.g.*, calcium sulphite) react very slowly, and must be in a very fine state of division.

For practice, the student may determine the percentage of $Na_2SO_3,7H_2O$ in the ordinary or A.R. crystallised product.

Procedure. Weigh out accurately about 0·25 g. of crystallised sodium sulphite (1), and add it to a 350 ml. conical flask containing 25 ml. of standard $0{\cdot}1N$ iodine, 5 ml. of $2N$ hydrochloric acid and 150 ml. of water. Swirl or stir the liquid until all the solid has reacted, and titrate the excess of iodine against standard $0{\cdot}1N$ sodium thiosulphate with starch as indicator. Repeat the determination with two other 0·25 g. portions of the sulphite.

Calculate the percentage of $Na_2SO_3,7H_2O$ in the sample employed.

$$1 \text{ Ml. } N \text{ I} \equiv 0{\cdot}03203 \text{ g. } SO_2 \equiv 0{\cdot}1261 \text{ g. } Na_2SO_3,7H_2O.$$

Note. 1. Alternatively, weigh out accurately about 2·5 g. of crystallised sodium sulphite, dissolve it in boiled-out water, and make the solution up to 250 ml. in a volumetric flask with boiled-out water. Shake well. Use 25 ml. for each titration.

III, 119. Determination of hydrogen sulphide and sulphides.—*Discussion.* The iodimetric method utilises the reversible reaction :

$$H_2S + I_2 \rightleftharpoons 2HI + S.$$

For reasonably satisfactory results, the sulphide solution must be dilute (concentration not greater than 0·04 per cent or 0·02*N*), and the sulphide solution added to excess of acidified 0·01*N* or 0·1*N* iodine and not conversely. Loss of hydrogen sulphide is thus avoided, and side reactions are almost entirely eliminated. (With solutions more concentrated than about 0·02*N*, the precipitated sulphur encloses a portion of the iodine, and this escapes the subsequent titration with the standard sodium thiosulphate solution.) The excess of iodine is then titrated against standard thiosulphate solution, using starch as indicator.

$$1 \text{ Ml. } N \text{ I} \equiv 0{\cdot}01703 \text{ g. } H_2S$$

Excellent results are obtained by the following method, which is of wider applicability. When excess of standard sodium arsenite solution is treated with hydrogen sulphide solution and then acidified with hydrochloric acid, arsenious sulphide is precipitated :

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The excess of arsenious acid is determined with 0·1*N* iodine and starch (compare Section **III, 104A**).

For practice, the student may determine the strength of hydrogen sulphide water.

Procedure. Prepare a saturated solution of hydrogen sulphide by bubbling the gas through distilled water. Place 50 ml. of standard 0·1*N* sodium arsenite into a 250 ml. volumetric flask, add 20 ml. of the hydrogen sulphide water, mix well, and add sufficient hydrochloric acid to render the solution distinctly acid. A yellow precipitate of arsenious sulphide is formed, but the liquid itself is colourless. Make up to the mark with distilled water, and shake thoroughly. Filter the mixture through a dry filter paper into a dry vessel. Remove 100 ml. of the filtrate, neutralise it with sodium bicarbonate, and titrate against standard 0·1*N* iodine and starch to the first blue colour. The quantity of residual arsenious acid is thus determined, and is deducted from the original 50 ml. employed.

Calculate the concentration of the hydrogen sulphide in the solution.

$$1 \text{ Ml. } N \text{ } As_2O_3 \equiv 0{\cdot}02556 \text{ g. } H_2S.$$

III. 120. Determination of ferricyanides.—*Discussion.* The reaction between ferricyanides and potassium iodide is a reversible one :

$$2K_3[Fe(CN)_6] + 2KI \rightleftharpoons 2K_4[Fe(CN)_6] + I_2,$$

but proceeds quantitatively from left to right in a slightly acid medium in the presence of a zinc salt. The very sparingly soluble potassium zinc ferrocyanide is formed :

$$2K_4[Fe(CN)_6] + 3ZnSO_4 = K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4,$$

and the ferrocyanide ions are thus removed from the sphere of action.

For practice, the student may determine the purity of potassium ferricyanide, preferably of A.R. grade.

Procedure. Weigh out accurately about 10 g. of the potassium ferricyanide and dissolve it in 250 ml. of water in a volumetric flask. Pipette 25 ml. of this solution into a 250 ml. conical flask, add about 20 ml. of 10 per cent potassium iodide solution, 2 ml. of $2N$ sulphuric or hydrochloric acid, and 15 ml. of a solution containing 2·0 g. of crystallised zinc sulphate. Titrate the liberated iodine immediately with standard $0{\cdot}1N$ sodium thiosulphate and starch ; add the starch solution (2 ml.) after the colour has faded to a pale yellow. The titration is complete when the blue colour has just disappeared. When great accuracy is required, the process should be conducted in an atmosphere of carbon dioxide. Repeat the titation with two other 25 ml. portions of the solution.

Calculate the purity of the salt.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}3293 \text{ g. } K_3[Fe(CN)_6].$$

III, 121. Determination of ferric iron (iodometric method). The reaction :

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2$$

is quantitative to the right hand side if the iodine is removed by titration with sodium thiosulphate solution, but is normally too slow to be of practical utility. The addition of a little cuprous iodide, however, acts as a catalyst and so accelerates the reaction that titration may be carried out forthwith. The cuprous iodide is prepared as follows. About 1 ml. of N copper sulphate solution is treated with an excess of 10 per cent potassium iodide solution (2 to 3 ml.) and the free iodine is discharged by the addition of aqueous sodium thiosulphate in the presence of starch solution. The precipitate is first thoroughly washed by decantation, and then shaken with 20 ml. of water ; about 1 ml. of the suspension thus obtained is used for a titration.

The slightly acid ferric solution, containing about 0·15 g. of Fe, is treated with 1 ml. of the cuprous iodide suspension and 10 per cent potassium iodide solution, and shaken well. After 3 to 5 minutes the whole is titrated with standard 0·1*N* sodium thiosulphate to the disappearance of the blue starch colour. The end point is fairly definite and permanent, although the starch colouration reappears more rapidly than in the copper-thiosulphate titration (Sections **III, 105-106**).

$$1 \text{ Ml. } N \ Na_2S_2O_3 \equiv 0{\cdot}05584 \text{ g. Fe.}$$

Note. If A.R. ferric alum is employed, the method will serve as a useful check for the standardisation of thiosulphate solutions.

OXIDATIONS WITH POTASSIUM IODATE

III, 122. General discussion.—A glance at the table of standard oxidation potentials (Table XVI, Section **I, 46**) reveals the fact that both potassium iodate and potassium bromate are stronger oxidising agents than iodine. The reaction between potassium iodate and reducing agents, such as potassium iodide or arsenious oxide, in weakly acidic solutions, say 0·1 to 2·0*N* hydrochloric acid, stops at the stage when the iodate is reduced to iodine :

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O\,;$$
$$2KIO_3 + 5H_3AsO_3 + 2HCl = 2KCl + 5H_3AsO_4 + I_2 + H_2O.$$

Actually the iodate is first reduced to iodide, and the latter is subsequently converted into free iodine. This can readily be shown by carrying out the oxidation of reducing substances in weak acid solutions (0·1 to 2*N* hydrochloric acid) containing mercuric sulphate ; here the iodide is converted into the fairly stable complex ion $[HgI_4]^{--}$ as fast as it is formed, and the reaction is accordingly arrested at the iodide stage. An example is :

$$4KIO_3 + 12H_3AsO_3 + HgSO_4\ (+\ HCl)$$
$$= K_2SO_4 + K_2[HgI_4] + 12H_3AsO_4\ (+\ HCl).$$

In more concentrated hydrochloric acid solutions (exceeding 4*N*) L. W. Andrews (1903) has shown that the iodate is reduced ultimately to iodine monochloride—the substance therefore acts as a very much more powerful oxidising agent. Examples are* :

$$KIO_3 + 2KI + 6HCl = 3KCl + 3ICl + 3H_2O\,;$$
$$KIO_3 + 2H_3AsO_3 + 2HCl = 2H_3AsO_4 + KCl + ICl + H_2O\,;$$
$$KIO_3 + 2I_2 + 6HCl = KCl + 5ICl + 3H_2O.$$

In these reactions the iodine which is initially liberated is converted into iodine chloride. Now both iodine and iodine chloride are brownish-yellow in aqueous solution, but in organic solvents, such as carbon tetrachloride or chloroform, iodine is purple whilst iodine chloride remains yellow. The point at which the last trace of iodine disappears may be determined by the change in colour from purple to yellow when a few ml. of carbon tetrachloride or chloroform are shaken up in the solution during the titration (compare Section **I, 71** and Section **III, 100**).

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* These equations give the final products only.

The use of potassium iodate in the presence of high concentrations of hydrochloric acid forms the basis of the Andrews procedure for the determination of reducing agents. It has been applied by G. S. Jamieson (1926)* and others to numerous quantitative determinations. Essentially, all methods depend upon the reaction :

$$I^- - 2\epsilon \rightleftharpoons I^+,$$

and conditions are so chosen as to stabilise the iodine cation. In the Andrews procedure, the experimental conditions are such that iodine chloride ($ICl \rightleftharpoons I^+ + Cl^-$†) is stable and its hydrolysis is repressed :

$$HCl + HIO \rightarrow ICl + H_2O \text{ (or } H^+ + HIO \rightarrow I^+ + H_2O).$$

Let us write down the ionic equations for the various stages in the reduction of iodate under the Andrews' conditions :

$IO_3^- + 6H^+ + 6\epsilon = I^- + 3H_2O,$

or $10IO_3^- + 60H^+ + 60\epsilon = 10I^- + 30H_2O$;

$IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O,$

or $2IO_3^- + 12H^+ + 10I^- = 6I_2 + 6H_2O$;

$IO_3^- + 6H^+ + 2I_2 = 5I^+ + 3H_2O,$

or $3IO_3^- + 18H^+ + 6I_2 = 15I^+ + 9H_2O.$

Upon addition, we have :

$$15IO_3^- + 90H^+ + 60\epsilon = 15I^+ + 45H_2O,$$

or

$$IO_3^- + 6H^+ + 4\epsilon = I^+ + 3H_2O.$$

Hence *under these particular conditions* the equivalent weight of potassium iodate is $KIO_3/4$, or a $0{\cdot}1N$ solution of potassium iodate will contain $KIO_3/4 \times 10$, or 214·02/40, or 5·3505 g. per litre.‡

Other methods for stabilising the iodine cation have been used and give, in most instances, equally satisfactory results. The most important of these is that due to R. Lang (1922 →) in which cyanide ions are used ; in the latter case the acidity should be slightly greater than N, and may be provided by either hydrochloric or sulphuric acid. Here iodine cyanide gives the necessary stability :

$$I^+ + CN^- \rightleftharpoons ICN.$$

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* G. S. Jamieson, *Volumetric Iodate Methods*, 1926 (Chemical Catalog Co., N.Y.)

† The following reaction may occur :

$$I^+ + 2Cl^- \rightleftharpoons ICl_2^-.$$

‡ The same result can be deduced from the hypothetical equation :

$$KIO_3 + 2HCl = KCl + ICl + H_2O + 2O.$$

The similarity between the Andrews' hydrochloric acid method and Lang's cyanide method may be illustrated by the stoicheiometric equations for the determination of iodides:

$$HIO_3 + 2HI + 3HCl = 3ICl + 3H_2O;$$
$$HIO_3 + 2HI + 3HCN = 3ICN + 3H_2O.$$

In view of the highly poisonous character of hydrogen cyanide, flasks with long and narrow necks must be used in all processes employing the "iodine cyanide" method. Only the "iodine chloride" procedure will, however, be described in this book.*

Potassium iodate, as already pointed out in Section **III, 102A,** is available commercially in a high state of purity, is anhydrous, can be dried at 120°C, and is stable in solution. The A.R. product has an assay value of better than 99·9 per cent. The titrations are carried out in glass-stoppered bottles or flasks of 250 or 300 ml. capacity in the presence of a high concentration of hydrochloric acid, otherwise hydrolysis of the iodine monochloride is liable to occur. The solution to be titrated should contain so much hydrochloric acid that, even after all the titrating solution has been added, the acidity is at least $4N$; that is, at least one-third, and preferably one-half, of the solution should consist of concentrated acid. The end point is detected by the loss of the last trace of purple (violet) colour from a layer of 5 ml. of chloroform or carbon tetrachloride when shaken with the liquid. When a titration has actually been completed, there is no return of the iodine colour even after keeping the solution for a day. Iodate titrations can be made in the presence of filter paper, alcohol, formaldehyde, saturated organic acids, as well as many other kinds of organic matter.

III, 123. Preparation of 0·1N (0·025M) potassium iodate.— Dry some A.R. potassium iodate at 120°C for 1 hour and allow it to cool in a desiccator. Weigh out exactly 5·351 g. of the finely-powdered potassium iodate on a watch glass, and transfer it by means of a clean camel hair brush directly into a dry 1 litre volumetric flask. Add about 400 to 500 ml. of water, and gently rotate the flask until the salt is completely dissolved. Make up to the mark with distilled water. Shake well. The solution will keep indefinitely.

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* For details of Lang's cyanide method, see A. D. Mitchell and A. M. Ward, *Modern Methods in Quantitative Chemical Analysis*, 1932, p. 6 (Longmans, Green and Co.); also W. Böttger-R. E. Oesper, *Newer Methods of Volumetric Chemical Analysis*, 1938, p. 76 (Van Nostrand and Co. or Chapman and Hall), and F. Sutton-A. D. Mitchell, *A Systematic Handbook of Volumetric Analysis*, 1935 (J. and A. Churchill).

It must be emphasised again that the solution is 0·1*N* only for the reaction :

$$IO_3^- + 6H^+ + 4\epsilon = I^+ + 3H_2O.$$

ANALYSES INVOLVING THE USE OF POTASSIUM IODATE SOLUTIONS.

III, 124. Determination of iodides.—This estimation is based upon the reaction :

$$IO_3^- + 6H^+ + 2I^- = 3I^+ + 3H_2O$$

$$(\text{or, } e.g., KIO_3 + 6HCl + 2KI = 3KCl + 3ICl + 3H_2O).$$

Thus 1 ml. 0·025*M* $KIO_3 \equiv 0{\cdot}006347$ g. I^- (since $KIO_3 \equiv 2I^-$).

For practice, the student may determine the percentage of iodine in potassium iodide.

Weigh out accurately about 2·0 g. of potassium iodide, and dissolve it in 250 ml. of water in a standard flask. Shake well. Transfer 25 ml. of this solution by means of a pipette into a stoppered reagent bottle of about 250 ml. capacity,* and add 25 ml. of water, 60 ml. of concentrated hydrochloric acid together with about 5 ml. of carbon tetrachloride or chloroform. Cool to room temperature. Run in the standard 0·1*N* potassium iodate from a burette until the solution, which at first is strongly coloured with iodine, becomes pale brown. The bottle is then stoppered and vigorously shaken, and the solvent layer acquires the purple colour due to iodine. Continue to add small volumes of the iodate solution, shaking vigorously after each addition, until the organic layer is only very faintly violet. Continue the addition dropwise, with shaking after each drop, until the solvent loses the last trace of violet and has only a very pale yellow colour (due to iodine chloride). The end point is very sharp and, after a little experience, is rarely overshot. If this should occur, a small volume of the iodide solution is added from a graduated pipette, and the end point re-determined. Repeat the titration with two other 25 ml. portions of the iodide solution.

Calculate the percentage of iodine in the sample of potassium iodide.

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* Alternatively, a 250 ml. measuring flask with a short neck and a well-fitting ground glass stopper may be used. The colour of the organic layer is readily seen by inverting the flask so that the layer of indicator collects in the neck.

Note. Iodine is similarly determined :

$$IO_3^- + 6H^+ + 2I_2 = 5I^+ + 2H_2O,$$

or, *e.g.*, $KIO_3 + 6HCl + 2I_2 = KCl + 5ICl + 3H_2O$.

Hence 1 ml. 0·025*M* $KIO_3 \equiv$ 0·01279 g. I, since $KIO_3 \equiv 2I_2$.

A mixture of iodine and iodide is estimated by first titrating the iodine with standard sodium thiosulphate solution, and then determining the iodine + iodide in a fresh portion with potassium iodate.

III, 125. Determination of arsenic or of antimony.—*Discussion.* The determination of arsenic in arsenious compounds is based upon the following reactions :

$$KIO_3 + As_2O_3 + 2HCl = KCl + As_2O_5 + ICl + H_2O$$

(*i.e.*, $IO_3^- + As_2O_3 + 2H^+ = I^+ + As_2O_5 + H_2O$) ;

or $KIO_3 + 2AsCl_3 + 5H_2O = KCl + 2H_3AsO_4 + ICl + 4HCl$.

Similar reactions occur with antimonious compounds.

Thus 1 ml. 0·025*M* $KIO_3 \equiv$ 0·003746 g. As $\equiv$ 0·006088 g. Sb.

Iron and copper do not interfere with these estimations.

For practice, the student may determine the percentage of As_2O_3 in commercial arsenious oxide or in the A.R. product.

Procedure. Weigh out accurately about 1·1 g. of arsenious oxide, dissolve this in a small quantity of warm 10 per cent sodium hydroxide solution, and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of this solution to a 250 ml. stoppered reagent bottle, add 25 ml. of concentrated hydrochloric acid and 5 ml. of carbon tetrachloride. Titrate with the standard 0·1*N* potassium iodate, as detailed in Section **III, 124,** until the iodine colour in the organic layer has disappeared. Allow to stand for 10 minutes, and observe whether the carbon tetrachloride shows any purple colour. If no colour is seen, the titration is complete. The acidity of the entire mixture at the end of the titration should not be less than 3*N* and not more than 5*N* ; with too high acidity the reaction takes place very slowly. Repeat the titration with two other 25 ml. portions of the solution.

Calculate the percentage of As_2O_3 in the sample.

III, 126. Determination of copper.—*Discussion.* The copper is precipitated as cuprous thiocyanate, and then titrated with standard potassium iodate solution in the presence of strong hydrochloric acid and a carbon tetrachloride or chloroform indicator. The reaction proceeds according to the following equation :

$$7KIO_3 + 2Cu_2(CNS)_2 + 14HCl \\ = 7KCl + 4CuSO_4 + 7ICl + 4HCN + 5H_2O.$$

Thus $7KIO_3 \equiv 4Cu$, or 1 ml. 0·025*M* $KIO_3 \equiv$ 0·009081 g. Cu.

The method may be applied to ores and certain alloys of copper ; the nitric acid employed for bringing the substance into solution must be expelled by evaporating with concentrated sulphuric acid to copious fuming.

For practice, the student may determine the percentage of copper in crystallised copper sulphate, preferably of A.R. grade. About 0·02 g. of copper is a suitable quantity for titration with 0·025*M* potassium iodate.

Procedure. Weigh out accurately about 0·8 g. of crystallised copper sulphate $CuSO_4,5H_2O$, dissolve it in water, add 5 ml. of *N* sulphuric acid, and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. to a conical flask, add 10 to 15 ml. of freshly-prepared saturated sulphurous acid solution, heat to boiling and add 10 per cent ammonium thiocyanate solution, slowly and with constant stirring, from a burette until further addition produces no change in colour, and add 3 to 4 ml. in excess (5 to 10 ml. in all). Allow the precipitate to settle for 10 to 15 minutes, filter through a quantitative filter paper or through a Gooch crucible with asbestos. Wash with a cold 1 per cent ammonium sulphate solution until free from thiocyanate. Transfer the washed precipitate with the filter paper or with the asbestos quantitatively into a 250 ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform or carbon tetrachloride. Add the 0·1*N* potassium iodate rapidly whilst rotating the bottle in order to keep the contents mixed. When the iodine has just disappeared from the solution, insert the stopper and shake thoroughly. The organic layer will be strongly coloured. From this point, continue the titration slowly, shaking the closed bottle after each addition of the iodate solution until the iodine colour has disappeared from the carbon tetrachloride or chloroform layer ; this marks the end point. Repeat with two other 25 ml. portions of the solution.

Calculate the percentage of copper in the sample used.

III, 127. Determination of mercury.—*Discussion.* The mercury is precipitated as mercurous chloride. The latter reacts with potassium iodate solution under the usual conditions in accordance with the equation :

$$KIO_3 + 2Hg_2Cl_2 + 6HCl = KCl + 4HgCl_2 + ICl + 3H_2O.$$

Thus $KIO_3 \equiv 4Hg \equiv 2Hg_2Cl_2$,

and 1 ml. 0·025*M* $KIO_3 \equiv$ 0·02006 g. Hg $\equiv$ 0·02361 g. Hg_2Cl_2.

For practice, the student may determine the percentage of mercury in mercuric chloride, preferably of A.R. quality.

Procedure. Weigh out accurately about 2·5 g. of finely-powdered mercuric chloride, and dissolve it in 100 ml. of water in a measuring flask. Shake well. Transfer 25 ml. of the solution to a conical flask, add 25 ml. of water, 2 ml. of *N* hydrochloric acid, and excess of 50 per cent phosphorous acid solution. Stir thoroughly and allow to stand for 12 hours or more. Flter the precipitated mercurous chloride through a quantitative filter paper or through a Gooch crucible with asbestos, and wash the precipitate moderately with cold water. Transfer the precipitate with the filter paper or asbestos quantitatively to a 250 ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Titrate the mixture with standard 0·1*N* potassium iodate in the usual manner (Section **III, 124**).

Calculate the percentage of mercury in the sample.

III, 128. Determination of tin.—*Discussion.* Potassium iodate solution reacts quantitatively with stannous chloride in the presence of concentrated hydrochloric acid in accordance with the equation :

$$KIO_3 + 2SnCl_2 + 6HCl = KCl + 2SnCl_4 + ICl + 3H_2O,$$

or $$IO_3^- + 2Sn^{++} + 6H^+ = 2Sn^{++++} + I^+ + 3H_2O.$$

Thus $KIO_3 \equiv 2Sn$, or 1 ml. 0·025*M* $KIO_3 \equiv$ 0·005935 g. Sn. This method possesses several advantages. The end point is very sharp. Extreme precautions need not be taken to prevent atmospheric oxidation if the bulk of the iodate solution is added rapidly at first ; the titration can then be completed at leisure. The method cannot be applied in the presence of antimony, cuprous and ferrous salts or precipitated metals ; these interfering substances can, however, be simply removed.

For practice, the student may determine the percentage of tin in hydrated stannous chloride, preferably of A.R. grade.

Procedure. Weigh out accurately about 1·5 g. of crystallised stannous chloride $SnCl_2,2H_2O$, dissolve it in concentrated hydrochloric acid, and make up to 250 ml. in a volumetric flask. Shake thoroughly. Remove 25 ml. of the solution to a 250 ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Add standard $0{\cdot}1N$ potassium iodate rapidly at first, whilst shaking the bottle to give the contents a gentle rotary motion, until the iodine colour, which gradually appears, has increased to the maximum intensity, then insert the stopper, and shake the solution thoroughly. Continue the titration slowly, shaking after each addition, until the organic layer is no longer blue. Repeat the titration with two other 25 ml. portions of the solution.

Calculate the percentage of tin in the sample.

III, 129. Determination of peroxides (lead, barium, and manganese dioxides).—*Discussion.* The method employed is an indirect one. Excess of potassium iodide solution, which has been standardised against potassium iodate (Section **III, 124**), is added to a weighed amount of the dioxide, and the mixture is titrated in the usual manner with standard potassium iodate solution, using chloroform or carbon tetrachloride as indicator. The reactions which occur are :

$$2MO_2 + 2KI + 8HCl = 2MCl_2 + 2KCl + 2ICl + 4H_2O$$

(where M = Pb, Mn or Ba)

$$i.e.,\ 2MO_2 + 2I^- + 8H^+ = 2M^{++} + 2I^+ + 4H_2O\ (\textit{oxidation})\ ;$$

$$KIO_3 + 2KI + 6HCl = 3KCl + 3ICl + 3H_2O,$$

$$i.e.,\ IO_3^- + 2I^- + 6H^+ = 3I^+ + 3H_2O\ (\textit{back titration}).$$

Now $MO_2 \equiv KI$, so that when the excess of iodide is determined by titration with the iodate, the percentage of MO_2 in the sample can be readily calculated. Any organic matter which may be present does not interfere with the estimation.

For practice, the student may determine the percentage of PbO_2 in the commercial dioxide.

Procedure. Weigh out accurately about 0·4 g. of lead dioxide into a 250 ml. reagent bottle ; it may be washed into the bottle with a little water. Add 25 ml. of $0{\cdot}1N$ potassium iodide and a volume of concentrated hydrochloric acid equal to the volume of liquid already in the bottle. Insert the stopper, and shake until all the lead dioxide has dissolved. Titrate the excess of potassium iodide with standard $0{\cdot}1N$ potassium iodate as described in Section **III, 124**. Titrate the potassium iodide solution against the standard potassium iodate solution, and thence compute the amount of potassium iodide which has reacted with the lead dioxide.

Calculate the percentage of PbO_2 in the sample.

III, 130. Determination of hydrogen peroxide.—*Discussion.* The method depends upon the interaction of dilute hydrogen peroxide solution with excess of standard sodium arsenite solution in the presence of sodium hydroxide :

$$As_2O_3 + 2H_2O_2 = As_2O_5 + 2H_2O.$$

The excess of sodium arsenite is then determined by titration with potassium iodate as detailed in Section **III, 125** :

$$KIO_3 + As_2O_3 + 2HCl = KCl + As_2O_5 + ICl + H_2O,$$

or $$IO_3^- + As_2O_3 + 2H^+ = I^+ + As_2O_5 + H_2O.$$

The amount of arsenite, found by titration, is deducted from that originally taken. Since $As_2O_3 \equiv 2H_2O_2$, the percentage of hydrogen peroxide in the original solution can be readily calculated. This method, like that of Section **III, 110,** is not influenced by the presence of organic preservatives.

Procedure. Dilute 25 ml. of "20 volume" hydrogen peroxide to 250 ml. in a volumetric flask. Place 50 ml. of $0{\cdot}1N$ sodium arsenite (Section **III, 104A**) and 10 ml. of 10 per cent sodium hydroxide solution into a 250 ml. reagent bottle, and add 25 ml. of the diluted hydrogen peroxide solution slowly from a burette whilst the contents of the bottle are gently rotated. Allow the mixture to stand for 2 minutes, and cautiously add 50 ml. of concentrated hydrochloric acid. Insert the glass stopper and, whilst holding it down firmly, shake the bottle vigorously. Release the stopper carefully so as to allow the excess of pressure of carbon dioxide to escape without losing any of the solution. Add 5 ml. of chloroform or of carbon tetrachloride, and titrate the unoxidised arsenious acid with standard $0{\cdot}025M$ potassium iodate. Repeat the titration with two other 25 ml. portions of the diluted hydrogen peroxide solution.

Titrate 25 ml. of the arsenite solution against the standard potassium iodate solution (Section **III, 125**). Calculate the volume of the arsenite solution which has reacted with the hydrogen peroxide, and thence the percentage of H_2O_2 in the original solution.

$$1 \text{ Ml. } N\ As_2O_3 \equiv 0{\cdot}01701 \text{ g. } H_2O_2.$$

III, 131. Determination of hydrazine.—*Discussion.* Hydrazine reacts with potassium iodate under the usual Andrews conditions thus :

$$KIO_3 + N_2H_4 + 2HCl = KCl + N_2 + ICl + 3H_2O,$$

or $IO_3^- + N_2H_4 + 2H^+ = I^+ + N_2 + 3H_2O.$

Thus $KIO_3 \equiv N_2H_4$,

or 1 ml. $0{\cdot}025M$ $KIO_3 \equiv 0{\cdot}0008013$ g. $N_2H_4 \equiv 0{\cdot}003253$ g. N_2H_4, H_2SO_4.

As an exercise, the student may determine the N_2H_4,H_2SO_4 content of hydrazine sulphate, preferably of A.R. quality.

Procedure. Weigh out accurately 0·08 to 0·1 g. of hydrazine sulphate into a 250 ml. reagent bottle, add a mixture of 30 ml. of concentrated hydrochloric acid, 20 ml. of water and 5 ml. of chloroform or carbon tetrachloride. Run in the standard $0{\cdot}025M$ potassium iodate slowly from a burette, with shaking between the additions, until the organic layer is just decolourised.

Calculate the percentage of N_2H_4,H_2SO_4 in the sample.

III, 132. Determination of thallium.—*Discussion.* Thallous salts are oxidised by potassium iodate under the Andrews conditions in accordance with the following equation :

$$KIO_3 + 2TlCl + 6HCl = KCl + 2TlCl_3 + ICl + 3H_2O,$$

i.e., $IO_3^- + 2Tl^+ + 6H^+ = I^+ + 2Tl^{+++} + 3H_2O.$

Thus $KIO_3 \equiv 2Tl$, or 1 ml. $0{\cdot}025M$ $KIO_3 \equiv 0{\cdot}01022$ g. Tl.

Procedure. Place 20 ml. of the solution containing 0·25 to 0·3 g. of thallium (*e.g.*, as thallous nitrate) into a 250 ml. reagent bottle, add 60 ml. of concentrated hydrochloric acid and 5 ml. of chloroform or carbon tetrachloride. Titrate with standard $0{\cdot}025M$ potassium iodate in the usual manner (Section **III, 124**) until the violet colour of the organic layer just vanishes.

Calculate the thallium content of the solution.

III, 133. Determination of iodides by means of ceric sulphate.—*Discussion.* This estimation utilises an application of Andrews' principle (Section **III, 122**), the iodide being oxidised to iodine chloride, ICl ($\rightleftharpoons I^+ + Cl^-$) :

$$I^- + 2Ce^{++++} = I^+ + 2Ce^{+++}.$$

The concentration of hydrochloric acid at the end of the titration should exceed $4N$, *i.e.*, two-fifths of the final volume of liquid should consist of concentrated acid.

For practice in this estimation, the student may determine the percentage of iodine in potassium iodide, preferably of A.R. quality.

Procedure. Weigh out accurately about 2·0 g. of potassium iodide, dissolve it in water, and make up to 250 ml. in a standard flask. Place 25 ml. of this solution and 50 ml. of concentrated hydrochloric acid in a 250 ml. glass-stoppered reagent bottle containing 5 ml. of carbon tetrachloride. Add standard 0·1*N* ceric sulphate (Sections **III, 74, 75**) from a burette with frequent shaking until the colour of the iodine is discharged from the solvent layer. Repeat the titration with two other 25 ml. portions of the iodide solution.

Calculate the percentage of iodine in the sample.

$$1 \text{ Ml. } N\ Ce(SO_4)_2 \equiv 0{\cdot}06346 \text{ g. I.}$$

III, 134. Determination of vanadium with potassium iodate. —*Discussion.* Vanadates are reduced by iodides in strongly acid (hydrochloric) solution in an atmosphere of carbon dioxide to the quadrivalent condition :

$$2H_3VO_4 + 2HI + 4HCl = 2VOCl_2 + I_2 + 6H_2O.$$

The liberated iodine and the excess of iodide is determined by titration with standard potassium iodate solution ; the hydrochloric acid concentration must not be allowed to fall below 7*N* in order to prevent re-oxidation of the vanadium compound by iodine chloride.

$$HIO_3 + 2I_2 + 5HCl = 5ICl + 3H_2O;$$
$$HIO_3 + 2HI + 3HCl = 3ICl + 3H_2O.$$

The total result of the reaction is :

$$4H_3VO_4 + 4HI + HIO_3 + 13HCl = 4VOCl_2 + 5ICl + 15H_2O,$$

and it can easily be shown that 1 ml. 0·025*M* $KIO_3 \equiv$ 0·005095 g. V.

This method is applicable in the presence of arsenate, phosphate or ferric iron, and also in the presence of tungstic acid, which may be held in solution by adding phosphoric acid.

Procedure. 25 Ml. of the solution containing 0·05 to 0·10 g. of vanadium (as vanadate) is placed in a 250 ml. glass-stoppered reagent bottle, and a rapid current of carbon dioxide is passed for 2 to 3 minutes into the bottle, but not through the solution. Sufficient concentrated hydrochloric acid is then added through a funnel to make the solution 6 to 8*N* during the titration. A known volume (excess) of approximately 0·05*M* potassium iodide, which has been titrated against the standard iodate solution (Section **III, 124**), is added. The whole is mixed, allowed to stand for 1 to 2 minutes, 5 ml. of carbon tetrachloride added, and then titrated as rapidly as possible with standard 0·025*M* potassium iodate until no more iodine colour can be detected in the organic layer. Concentrated hydrochloric acid should be added as needed during the titration so that the concentration does not fall below 7*N*.

OXIDATIONS WITH POTASSIUM BROMATE

III, 135. General discussion.—Potassium bromate is a powerful oxidising agent in acid solution (Table XVI, Section **I, 46**). Reducing agents convert it smoothly into the bromide :

$$BrO_3^- + 6H^+ + 6\epsilon = Br^- + 3H_2O.$$

The equivalent weight is therefore 1/6 mol ($KBrO_3/6$), or 167·02/6, or 27·84, and a 0·1*N* solution contains 2·784 g. potassium bromate per litre.* At the end of the titration free bromine appears :

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O.$$

The presence of free bromine, and consequently the end point, can be detected by its yellow colour, but it is better to use indicators such as methyl orange, methyl red or indigo-carmine. These indicators have their usual colour in acid solution, but are destroyed by the first excess of bromine and assume a pale yellow colour (yellow-green to yellow with a reddish tinge for indigo carmine). The colour change is not reversible, since, as already stated, the indicators are decomposed by the bromine. The quantity of bromate consumed by the indicator is exceedingly small and can be neglected for 0·1*N* solutions. Direct titration with bromate solution in the presence of irreversible dyestuff indicators are usually made in hydrochloric acid solution, the concentration of which should be at least 1·5 to 2*N*. At the end of the titration some chlorine may appear by virtue of the reaction :

$$10Cl^- + 2BrO_3^- + 12H^+ = 5Cl_2 + Br_2 + 6H_2O\,;$$

this immediately bleaches the indicator.

The titrations should be carried out slowly so that the indicator change, which is a time reaction, may be readily detected. If the determinations are to be executed rapidly, the volume of the bromate solution to be used must be known approximately, since ordinarily with irreversible dyestuff indicators there is no simple way of ascertaining when the end point is close at hand. Examples of estimations utilising direct titration with standard bromate are expressed by the following equations :

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* The same result can be obtained by considering the hypothetical equation:

$$HBrO_3 = HBr + 3O,$$

i.e., 1 mol of potassium bromate supplied 6 equivalents of oxygen.

$$KBrO_3 + 3H_3AsO_3\ (+ HCl) = KBr + 3H_3AsO_4\ (+ HCl);$$
$$KBrO_3 + 3SbCl_3 + 6HCl = KBr + 3SbCl_5 + 3H_2O;$$
$$KBrO_3 + 3SnCl_2 + 6HCl = KBr + 3SnCl_4 + 3H_2O;$$
$$2KBrO_3 + 3N_2H_4\ (+ HCl) = 2KBr + 3N_2 + 6H_2O\ (+ HCl);$$
$$KBrO_3 + NH_2OH\ (+ HCl) = KBr + HNO_3 + H_2O\ (+ HCl);$$
$$KBrO_3 + 6K_4[Fe(CN)_6] + 6HCl = KBr + 6K_3[Fe(CN)_6] + 6KCl + 3H_2O.$$

Various substances cannot be oxidised directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromide :

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O.$$

In this reaction one molecule of bromate yields six atoms of bromine, hence the equivalent weight is $KBrO_3/6$, identical with that of potassium bromate alone. Bromine is very volatile, and hence such operations should be conducted at as low a temperature as possible and in reagent bottles fitted with ground glass stoppers. The excess of bromine is determined iodimetrically—by the addition of excess of potassium iodide and titration of the liberated iodine with standard thiosulphate solution :

$$2KI + Br_2 = 2KBr + I_2.$$

Potassium bromate is readily available in a high state of purity ; the A.R. product has an assay value of at least 99·9 per cent. The substance can be dried at 120° to 150°C, is anhydrous, and the aqueous solution keeps indefinitely. It can therefore be employed as a primary standard. Its only disadvantage is that the equivalent weight is comparatively small.

III, 136. Preparation of 0·1*N* potassium bromate.—Dry some finely-powdered A.R. potassium bromate for 1 to 2 hours at 120°C, and allow to cool in a desiccator. Weigh out accurately 2·784 g. of the pure potassium bromate, and dissolve it in 1 litre of water in a volumetric flask.

ANALYSES INVOLVING THE USE OF STANDARD POTASSIUM BROMATE SOLUTIONS

III, 137. Determination of antimony or of arsenic.—*Discussion.* The antimony or the arsenic must be present in the trivalent condition. The reaction of trivalent arsenic or antimony with potassium bromate may be written:

$$2KBrO_3 + 3M_2O_3 + 2HCl \\ = 2KCl + 3M_2O_5 + 2HBr \quad (M = \text{As or Sb}).$$

$$\text{Hence } 1 \text{ ml. } N\ KBrO_3 \equiv 0{\cdot}04946\text{ g. } As_2O_3 \equiv 0{\cdot}03746\text{ g. As} \\ \equiv 0{\cdot}07288\text{ g. } Sb_2O_3 \equiv 0{\cdot}06088\text{ g. Sb}.$$

The presence of tin and of considerable quantities of iron and copper interfere with the estimations.

For practice in the use of potassium bromate solution, the student may (*a*) titrate standard 0·1*N* sodium arsenite against the standard bromate and (*b*) determine the percentage of antimony in tartar emetic.

Procedure. **Titration with standard sodium arsenite solution.** Place 25 ml. of standard 0·1*N* sodium arsenite (Section **III, 48,** *Procedure A*, Note 1 and Section **III, 104A**) into a conical flask, add 25 ml. of water, 15 ml. of concentrated hydrochloric acid, and 2 drops of methyl orange or methyl red indicator. Titrate slowly with the standard 0·1*N* potassium bromate with constant swirling of the solution. As the end point approaches, the bromate solution is added dropwise with intervals of 2 to 3 seconds between the drops until the colour changes sharply from red to colourless or very pale yellow. Add another drop of the indicator to make sure that the end point has been reached. Repeat the titration with two other 25 ml. portions of the arsenite solution.

Compare the volume of potassium bromate solution used with the calculated volume.

Procedure. **Antimony in tartar emetic.** Weigh out accurately about 4 g. of finely-powdered A.R. potassium antimonyl tartrate or 5 g. of tartar emetic, dissolve it in water, and make up to 250 ml. in a standard flask. Transfer 25 ml. of this solution to a conical flask, add 25 ml. of water, 15 ml. of concentrated hydrochloric acid, and a few drops of methyl orange or methyl red indicator. Add the standard 0·1*N* potassium bromate very slowly until the colour of the indicator is just discharged. Repeat the titration with two further 25 ml. portions of the solution.

Calculate the percentage of antimony in the sample.

III, 138. Determination of metals by means of 8-hydroxyquinoline (" oxine ").—*Discussion.* Various metals (*e.g.*, aluminium, iron, copper, zinc, cadmium, nickel, cobalt, manganese, and magnesium) under specified conditions of *p*H yield well-defined crystalline precipitates with 8-hydroxyquinoline. These precipitates have the general formula $Me(C_9H_6ON)_n$, where *n* is the valency of the metal (see, however, Section **I, 62L**). Upon treatment of the oxinates with dilute hydrochloric acid, the oxine is liberated. Oxine reacts with 4 equivalents of bromine to give 5 : 7-dibromo-8-hydroxyquinoline (R. Berg, 1926) :

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr.$$

Hence 1 mol of the oxinate of a divalent metal requires 8 equivalents of bromine, whilst that of a trivalent metal requires 12 equivalents. The bromine is derived by the addition of standard 0·1*N* potassium bromate and excess of potassium bromide to the acid solution.

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O.$$

Full experimental details are given below for the determination by the student of aluminium in potash alum and of magnesium in magnesium sulphate.

Of the other elements which may be estimated volumetrically with the aid of 8-hydroxyquinoline iron, copper (Sections **III, 106, 126**), cadmium (Section **III, 38**), zinc (Sections **III, 145, 38**), nickel (Sections **III, 42, 38**), cobalt (Section **III, 37**), and manganese (Section **III, 60**) may be determined by other more convenient and less expensive methods. Outlines of the procedures for cadmium, cobalt, nickel, titanium, zinc and zirconium* will be given.

Procedure A. **Determination of aluminium.** Prepare a 2 per cent solution of A.R. 8-hydroxyquinoline in 2*N* acetic acid (1) ; add ammonia solution until a permanent precipitate is just produced, and re-dissolve this by warming.

Weigh out accurately about 3·50 g. of potash alum $K_2SO_4,Al_2(SO_4)_3,24H_2O$, preferably of A.R. grade, and dissolve it in 250 ml. of water in a volumetric flask. Shake well. Transfer 25 ml. of the solution, which contains about 0·02 g. of Al, to a conical flask, add 125 ml. of water, and warm to 50° to 60°C. Then add a 20 per cent excess of the oxine solution (1 ml. will precipitate 0·001 g. of Al), when the complex $Al(C_9H_6ON)_3$ will be formed. Complete the precipitation by the addition of a solution of 40 g. of ammonium acetate in the minimum quantity of water, stir the mixture, and allow to cool. Filter the granular precipitate through a coarse-mesh sintered glass crucible (or through a porous porcelain crucible), and wash with hot water (2). Dissolve the complex in warm concentrated hydrochloric acid, or, better, in a mixture of equal volumes of 10 to 15 per cent hydrochloric acid and alcohol, collect the solution in a 250 ml. reagent bottle, add a few drops of indicator (0·1 per cent solution of the sodium salt of methyl red or 1 per cent indigo-carmine solution), and 0·5 to 1 g. of pure potassium bromide. Titrate slowly with standard 0·1*N* (*i.e.*, *M*/60) potassium bromate until the colour becomes pure yellow (with either indicator). The exact end point is not easy to detect, and it is better to add a slight excess of standard bromate solution (free bromine is thus present, and is tested for by removing a drop of the liquid on to potassium iodide-starch paper), diluting the solution considerably with 2*N* hydrochloric acid (to prevent the precipitation of 5 : 7-dibromo-8-hydroxyquinoline during the titration), then add 10 ml. of 10 per cent potassium iodide solution, and titrate the liberated iodine against standard 0·1*N* sodium thiosulphate, using starch as indicator (3). Repeat the titration with two other 25 ml. portions of the aluminium solution.

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* For other elements, see R. Berg, *Die Analytische Verwendung von O-Oxychinolin („ Oxin ") und Seiner Derivate*, 2nd Edition, 1938 (F. Enke).

From the above discussion, it is evident that Al ≡ 12Br., *i.e.*, to 12,000 ml. of 0·1*N* bromate (or 0·1*N* thiosulphate), hence

$$1 \text{ Ml. } N\ KBrO_3 \equiv 0{\cdot}002249 \text{ g. Al.}$$

Calculate the percentage of aluminium in the sample employed.

Notes. 1. An alcoholic solution cannot be used since the aluminium complex is slightly soluble in alcohol, nor can this solvent be used for washing the complex.

2. This will remove the excess of oxine. Complications due to adsorption of iodine will thus be avoided.

3. A brown additive compound of iodine with the dibromo compound may separate during the titration. It is, however, completely decomposed by the thiosulphate, so that it does not affect the end point.

Procedure B. **Determination of magnesium.** Weigh out accurately about 1·0 g. of crystallised magnesium sulphate, preferably of A.R. quality, and dissolve it in 250 ml. of water in a standard flask. Mix thoroughly. Pipette 25 ml. of this solution into a beaker, add 5 g. of ammonium acetate dissolved in 50 ml. of water, and heat to boiling. Add a slight excess of a 2 per cent solution of oxine in 2*N* acetic acid,[*] and then concentrated ammonia solution slowly and with stirring until the liquid is faintly alkaline (*e.g.*, to phenolphthalein paper). Boil the mixture for 1 or 2 minutes until the yellow precipitate becomes crystalline, and allow to settle. The supernatant liquid should be yellow indicating that an excess of reagent is present. Filter the precipitate through a sintered glass crucible (1*G*3, or through a porous porcelain crucible), and wash the precipitate thoroughly with hot water (1). Dissolve the precipitate on the filter in 2 to 3*N* hydrochloric acid, and wash the filter with the same acid until the washings are colourless. Transfer the filtrate and washings quantitatively to a reagent bottle or a glass-stoppered flask. Add 1 g. of pure potassium bromide, several drops of indicator (methyl red or indigo-carmine), and titrate against standard 0·1*N* potassium bromate as described under aluminium (*Procedure A*). The same difficulty in detecting the end point is experienced here also, and is overcome in a similar way. Repeat the titration with two other 25 ml. portions of the solution.

Calculate the percentage of magnesium in the sample.

$$1 \text{ Ml. } N\ \mathrm{KBrO_3} \equiv 0{\cdot}003040 \text{ g. Mg.}$$

Note. 1. The magnesium "oxinate" is appreciably soluble in hot water, hence washing is discontinued when the colour of the washings changes from a deep yellow to a pale yellow. It is probably better to employ a hot 1-2 per cent ammonia solution as the wash liquid (R. Berg, 1938).

Procedure C. **Determination of cadmium.** The solution (about 100 ml.; up to 0·1 g. Cd) of the metal is treated with sodium carbonate solution until faintly cloudy, and the turbidity is just removed by the addition of dilute acetic acid. The mixture is warmed to 60°C, 3 to 5 g. of sodium acetate are added (1), and a slight excess of a 2 per cent solution of oxine in alcohol stirred in, the supernatant liquor being then of a golden-yellow colour and the precipitate of $\mathrm{Cd(C_9H_6ON)_2,2H_2O}$ a pale yellow. The mixture is heated nearly to boiling, set aside for a few minutes, and then filtered on a sintered glass or porous porcelain crucible, washed with hot water (2), dissolved in moderately concentrated hydrochloric acid (say, 4*N*), and titrated with 0·1*N* potassium bromate (*Procedure A*).

$$1 \text{ Ml. } N\ \mathrm{KBrO_3} \equiv 0{\cdot}01405 \text{ g. Cd.}$$

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[*] **For details of the preparation of the reagent, see Section I, 62C.**

Note. 1. If copper is initially present, precipitation should be carried out in 10 per cent acetic acid solution without the addition of sodium acetate. The copper is thus completely precipitated as $Cu(C_9H_6ON)_2$*, and the cadmium remains in the filtrate, from which it is precipitated by neutralisation and the addition of sodium acetate. Furthermore, precipitation in the presence of potassium cyanide from sodium acetate solutions containing a trace of acetic acid ensures that mercury, if present, remains in solution.

2. For the **gravimetric determination of cadmium,** the precipitate is dried at 130°C and weighed as $Cd(C_9H_6ON)_2$, which contains 28·05 per cent Cd.

Procedure D. **Determination of cobalt.** The neutral or weakly acidic (acetic acid) solution† of the cobaltous salt (150 ml. ; up to 0·06 g. Co) containing sodium acetate (5 g.) is warmed to 70°C, treated with a slight excess of a 2 per cent alcoholic solution of oxine, and boiled gently until the light-brown amorphous cobalt oxinate $Co(C_9H_6ON)_2,2H_2O$ becomes crystalline. The latter is allowed to settle, filtered off on a sintered glass or porous porcelain crucible, washed with hot water, dissolved in fairly strong hydrochloric acid, and titrated with standard 0·1*N* potassium bromate (*Procedure A*).

$$1 \text{ Ml. } N \ KBrO_3 \equiv 0{\cdot}007368 \text{ g. Co.}$$

Procedure E. **Determination of nickel.** The solution of the nickelous salt (150 ml. ; up to 0·1 g Ni), containing 3 to 5 g. of sodium acetate and 8 to 10 per cent of acetic acid, is warmed to 70°C, treated with excess of 2 per cent alcoholic oxine solution, and then boiled until the precipitate of $Ni(C_9H_6ON)_2,2H_2O$ becomes granular. The whole is filtered through a sintered glass or porous porcelain crucible, the precipitate thoroughly washed with hot water, dissolved in hydrochloric acid, and titrated with 0·1*N* potassium bromate (*Procedure A*).

$$1 \text{ Ml. } N \ KBrO_3 \equiv 0{\cdot}007335 \text{ g. Ni.}$$

Note. This process affords a complete separation from manganese.

Procedure F. **Determination of titanium.** The solution (150 ml. ; up to 0·07 g. Ti) is treated with 1 g. of tartaric acid, 0·5 g. of sodium acetate, then with ammonia until barely alkaline to phenolphthalein, and finally with 1·5 ml. of glacial acetic acid. The solution is warmed to 60°C, stirred whilst excess of 2 per cent alcoholic oxine solution is added, and then boiled for 10 minutes to effect granulation of the titanium oxinate, $TiO(C_9H_6ON)_2,2H_2O$. The latter is then filtered off on a sintered glass or porous porcelain crucible, and washed with hot water (1). The precipitate is dissolved in 1 : 1 hydrochloric acid, and titrated by 0·1*N* potassium bromate and 0·1*N* sodium thiosulphate (*Procedure A*).

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* For the gravimetric determination of copper, the precipitate is dried at 105° to 110°C and weighed as $Cu(C_9H_6ON)_2$ which contains 18·07 per cent Cu.

† If mineral acid is present, sodium acetate is added.

$$1 \text{ Ml. } N \text{ KBrO}_3 \equiv 0{\cdot}005988 \text{ g. Ti.}$$

Note. 1. The excess of oxine is removed when the washings are colourless. To confirm this (or when in doubt) mix 25 ml. of the filtrate with 10 ml. of concentrated hydrochloric acid, add 2 drops of a a 0·2 per cent alcoholic solution of methyl red (or of the aqueous solution of the sodium salt) and a little potassium bromide solution ; the addition of 1 drop of 0·1*N* potassium bromate should result in decolourisation.

Procedure G. **Determination of zinc.** The solution should contain either (i) 5 g. of sodium or ammonium acetate and 4 g. of acetic acid or (ii) 5 g. of sodium tartrate and 25 ml. of *N* sodium hydroxide in 100 ml., and not more than 0·15 g. of zinc. In (i), the solution is warmed to 60°C, treated with a slight excess of a 2 per cent solution of oxine in 2*N* acetic acid or in alcohol, boiled for a few minutes, filtered and washed with hot water (1). In (ii), the solution is treated with a 2 per cent alcoholic solution of oxine in the cold, warmed at 60° until the precipitate becomes crystalline, and filtered. The well-washed precipitate (1) is dissolved in 2*N* hydrochloric acid and titrated with 0·1*N* potassium bromate (*Procedure A*).

$$1 \text{ Ml. } N \text{ KBrO}_3 \equiv 0{\cdot}008175 \text{ g. Zn.}$$

Note. 1. For the **gravimetric determination of zinc,** the precipitate is dried at 130° to 140°C and weighed as $Zn(C_9H_6ON)_2$, which contains 18·49 per cent Zn.

Procedure H. **Determination of zirconium.** Zirconium is precipitated by oxine from an acetate-buffered solution of the nitrate as $Zr(C_9H_6ON)_4$: the chloride and sulphate yield an " oxinate " approximating to the composition $ZrO(C_9H_6ON)_2$. The solution of zirconium nitrate in nitric acid should contain not more than 0·015 g. of Zr and be free from other elements which react with oxine. The solution is evaporated to a volume of a few ml. on the water bath, 10 ml. of nitric acid (sp. gr. 1·20) added and again evaporated to a small volume, but not to dryness. The solution is diluted to 150 ml., warmed to 50° to 60°C, 8 to 15 ml. of a 2 per cent alcoholic solution of oxine and 50 to 70 ml. of 2*N* ammonium acetate solution added with constant stirring. The solution is boiled until the precipitate is crystalline and pure yellow in colour. The precipitate is allowed to settle and whilst still warm filtered through a sintered glass crucible (1*G*4) or through a quantitative filter paper, washed with hot 1 per cent ammonium acetate solution until the washings are colourless, and then with cold water (1). The " oxinate " is dissolved in cold 1 : 1 sulphuric acid, the solution diluted to 150 ml. and titrated with 0·1*N* potassium bromate (*Procedure A*).

$$1 \text{ Ml. } N \text{ KBrO}_3 \equiv 0{\cdot}005701 \text{ g. Zr.}$$

Note. 1. For the **gravimetric determination of zirconium,** the precipitate is dried at 130° to 140°C and weighed as $Zr(C_9H_6ON)_4$, which contains 13·66 per cent Zr.

III, 139. Determination of hydroxylamine. The method based upon the reduction of ferric solutions in the presence of sulphuric acid, boiling, and subsequent titration in the cold with standard 0·1*N* potassium permanganate frequently yields high results unless the experimental conditions are closely controlled :

$$2NH_2OH + 2Fe_2(SO_4)_3 = 4FeSO_4 + 2H_2SO_4 + N_2O + H_2O.$$

$$1 \text{ Ml. } N \text{ KMnO}_4 \equiv 0{\cdot}01652 \text{ g. NH}_2\text{OH.}$$

The best results are obtained by oxidation with potassium bromate in the presence of hydrochloric acid :

$$NH_2OH + HBrO_3 = HNO_3 + HBr + H_2O.$$

The hydroxylamine solution is treated with a measured volume of 0·1*N* (*i.e.*, *M*/60) potassium bromate so as to give 10 to 30 ml. excess, followed by 40 ml. of 5*N* hydrochloric acid. After 15 minutes the excess of bromate is determined by the addition of potassium iodide solution and titration against standard 0·1*N* sodium thiosulphate (compare Section **III, 138**).

$$1 \text{ Ml. } N \text{ KBrO}_3 \equiv 0{\cdot}005505 \text{ g. NH}_2\text{OH.}$$

III, 140. General discussion. Preparation and standardisation of 0·1*N* solution.—Chloramine-T is the sodium derivative of *N*-chloro-*p*-toluenesulphonamide $CH_3.C_6H_4.SO_2NClNa,3H_2O$ (molecular weight, 281·70), and is obtainable commercially in a high state of purity; it is a by-product in the manufacture of saccharin. The aqueous solution reacts as if it were a hypochlorite, and it has the great advantage that it is far more stable than sodium hypochlorite solution:

$$CH_3.C_6H_4.SO_2NClNa + H_2O \rightleftharpoons CH_3.C_6H_4.SO_2NH_2 + NaOCl.$$

Chloramine-T was introduced as a volumetric reagent by A. Noll (1924) as a cheap substitute for iodine in the determination of trivalent arsenic and antimony. The reagent reacts in dilute acid (3 to 5 per cent) solution; if the acid is too concentrated, secondary changes occur.

Chloramine-T reacts with potassium iodide in acid solution to liberate iodine:

$$\begin{aligned}&CH_3.C_6H_4.SO_2NClNa + 2KI + 2HCl\\&\qquad = CH_3.C_6H_4.SO_2NH_2 + I_2 + NaCl + 2KCl.\end{aligned}$$

The equivalent weight is therefore 1/2 mol, or 281·70/2, or 140·85. Reaction also occurs quantitatively with arsenious acid:

$$\begin{aligned}&2CH_3.C_6H_4.SO_2NClNa + As_2O_3 + 2H_2O\\&\qquad = 2CH_3.C_6H_4.SO_2NH_2 + As_2O_5 + 2NaCl.\end{aligned}$$

Prepare an approximately 0·1*N* solution of chloramine-T by dissolving 14·5 g. of the purest commercial product in 1 litre of water. It may be standardised by one of two methods.

1. Treat 25 ml. of the chloramine-T solution with 2 ml. of 2*N* hydrochloric acid and 10 ml. of 10 per cent potassium iodide solution. Titrate the liberated iodine with standard 0·1*N* sodium thiosulphate in the usual way, using 2 ml. of starch as indicator.

2. Add the chloramine-T solution from a burette to 25 ml. of standard 0·1*N* arsenious oxide, containing a small crystal of pure potassium iodide and 1 ml. of starch solution, until a permanent blue colour just appears.

ANALYSES INVOLVING THE USE OF STANDARD CHLORAMINE-T SOLUTIONS

III, 141. Determination of antimony.—For practice in this estimation, the student may determine the percentage of antimony in tartar emetic or in A.R. potassium antimony tartrate.

Weigh out accurately about 0·35 g. of tartar emetic or of A.R. potassium antimonyl tartrate, and dissolve it in 100 ml. of water in a conical flask. Add 0·2 g. of tartaric acid, 1 g. of sodium bicarbonate, 2 ml. of starch solution, and a small crystal of pure potassium iodide. Titrate with the standard 0·1*N* chloramine-T to the first permanent blue colouration. Repeat the titration with two similar quantities of the antimony compound.

Calculate the percentage of antimony in the sample.

1 Ml. *N* chloramine-T ≡ 0·06088 g. Sb.

III, 142. Determination of nitrites.—For practice in this estimation, the student may determine the percentage purity of sodium nitrite, preferably of A.R. grade.

Weigh out accurately about 1·5 g. of sodium nitrite, and dissolve it in 500 ml. of boiled-out water in a volumetric flask. Shake thoroughly. Place 50 ml. of the standard chloramine-T solution in a conical flask, and transfer 25 ml. of the nitrite solution to the flask by means of a pipette, keeping the tip of the pipette below the surface of the liquid during the addition. Add a few ml. of dilute acetic acid. The sodium salt is decomposed with the separation of the corresponding free chloramine as a white cloud, which rapidly diminishes in intensity. After 2 minutes, add excess of 10 per cent potassium iodide solution, and titrate the liberated iodine with standard 0·1*N* sodium thiosulphate, using 2 ml. of starch solution as indicator. To another 50 ml. of the chloramine solution add potassium iodide solution and dilute acid, and titrate with the standard 0·1*N* sodium thiosulphate (Section **III, 140**) ; the difference between the two titres is a measure of the nitrite. Repeat the titration with two other 25 ml. portions of the nitrite solution.

$$NaNO_2 + CH_3.C_6H_4.SO_2NClNa + H_2O$$
$$= NaNO_3 + CH_3.C_6H_4.SO_2NH_2 + NaCl.$$

Now $CH_3.C_6H_4.SO_2NClNa \equiv 2Na_2S_2O_3 \equiv NaNO_2$, hence

1 ml. *N* $Na_2S_2O_3 \equiv 0{\cdot}02301$ g. $NO_2 \equiv 0{\cdot}03456$ g. $NaNO_2$.

Calculate the percentage of $NaNO_2$ in the sample.

III, 143. Determination of tin.—*Discussion.* The tin must be present in the stannous condition. Reduction is best effected in hydrochloric acid solution by means of pure aluminium (free from iron), pure zinc turnings, or pure lead foil. During the whole of the titration a continuous current of carbon dioxide should be maintained above the stannous solution, for this is very sensitive to atmospheric oxidation. The reaction between stannous solution and the chloramine-T is :

$$CH_3.C_6H_4.SO_2NClNa + SnCl_2 + 2HCl$$
$$= CH_3.C_6H_4.SO_2NH_2 + SnCl_4 + NaCl$$

hence 1 ml. *N* chloramine-T ≡ 0·05935 g. Sn.

For practice, the student may determine the percentage of tin in hydrated stannous chloride.

Procedure. Weigh out accurately about 2·5 g. of crystallised stannous chloride, preferably of A.R. quality, dissolve it in 150 ml. of concentrated hydrochloric acid, transfer to a 250 ml. volumetric flask, and make up to the mark with boiled-out distilled water. Shake well. Transfer 25 ml. of the solution (which contains about 0·15 g. Sn) into a 350 or 500 ml. conical flask, add 30 ml. of concentrated hydrochloric acid and 100 ml. of water, and finally pure lead foil to give a surface of about 24 square inches (or an equivalent quantity of A.R. lead granules). Insert a three-holed rubber stopper as detailed in Section **III, 116,** *Procedure B,* and pass a slow stream of carbon dioxide through the flask. Boil for 90 minutes and then allow to cool ; the current of gas is maintained throughout the reduction* and the subsequent titration. Add sufficient sodium hydroxide (14 to 15 g.), dissolved in air-free water, to reduce the free acid concentration to 3 to 5 per cent in order to avoid side reactions of the chloramine. Then add a crystal of potassium iodide, 2 ml. of starch solution, and titrate the mixture with standard 0·1*N* chloramine-T until the presence of the slightest excess is shown by the liberation of iodine and the appearance of the usual blue colour. Repeat the estimation with another 25 ml. portion of the solution.

Calculate the percentage of tin in the sample.

Note. If experience with a stannic salt is desired, stannic ammonium chloride (ammonium chlorostannate) may be used.

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* The reduction is not really essential in the present instance, but is described in order to illustrate the technique involved in other estimations, *e.g.*, tin in an alloy or in a stannic salt.

III, 144. Determination of ferrocyanides.—*Discussion.* Ferrocyanides are quantitatively oxidised by chloramine-T in weakly acid solution (2·5 per cent by volume of hydrochloric acid) :

$$CH_3.C_6H_4.SO_2NClNa + 2H^+ + 2[Fe(CN)_6]^{----}$$
$$= CH_3.C_6H_4.SO_2NH_2 + NaCl + 2[Fe(CN)_6]^{---}.$$

Excess of standard chloramine-T solution is added to the feebly acid solution of the ferrocyanide at 40°C ; the residual chloramine-T is determined by means of excess of standard sodium arsenite solution after the addition of sodium bicarbonate.

For practice, the student may determine the percentage purity of A.R. potassium ferrocyanide $K_4[Fe(CN)_6], 3H_2O$.

Weigh out accurately about 1 g. of A.R. potassium ferrocyanide, and dissolve it in 100 ml. of distilled water in a glass-stoppered conical flask. Warm to 40°C, and add 2·5 ml. of *N* hydrochloric acid. Add 50 ml. of standard 0·1*N* chloramine-T and mix thoroughly. Then introduce 1 to 1·5 g. of sodium bicarbonate, shake until dissolved, add a known volume (excess) of standard 0·1*N* sodium arsenite. Determine the excess of the latter by the addition of a crystal of potassium iodide, and 2 ml. of starch solution, followed by titration with the standard chloramine-T solution to the first permanent blue colour. Repeat with a similar quantity of potassium ferrocyanide.

Calculate the percentage purity of the sample.

1 Ml. *N* chloramine-T $\equiv$ 0·3684 g. $K_4[Fe(CN)_6]$.

MISCELLANEOUS VOLUMETRIC DETERMINATIONS

III, 145. Determination of zinc with standard potassium ferrocyanide solution.—*Discussion.* Zinc ions in neutral or acid medium react with potassium ferrocyanide solution to form the very sparingly soluble potassium zinc ferrocyanide :

$$3Zn^{++} + 2K_4[Fe(CN)_6] = K_2Zn_3[Fe(CN)_6]_2 + 6K^+.$$

Formerly the end point of the reaction was determined by means of external indicators, such as uranyl nitrate and ammonium molybdate. The acidified zinc solution was slowly titrated at 60° to 80°C with the ferrocyanide solution until a drop of the solution, brought into contact with a drop of uranyl nitrate solution on a white spot plate, gave a light brown colour (due to the formation of uranyl ferrocyanide). In recent years, the external indicator has been replaced by the more convenient internal indicator (diphenylamine, diphenylbenzidine, or sodium diphenylamine sulphonate). The latter substances are oxidation-reduction indicators, and are therefore dependent for their action upon the *ratio* of the concentration of ferricyanide to ferrocyanide in the solution (compare Section **I, 50**). A 0·05M potassium ferrocyanide solution, to which 0·3 g. of potassium ferricyanide per litre is added, is employed ; the solution is accordingly approximately 0·001M with respect to ferricyanide. The oxidation potential of a ferrocyanide-ferricyanide electrode is given by the equation (Section **I, 48**) :

$$E = E^\circ + 0{\cdot}0591 \log \frac{[\{Fe(CN)_6\}^{---}]}{[\{Fe(CN)_6\}^{----}]} \quad \text{(at 25°C)}.$$

As long as excess of zinc ions remain in solution, the concentration of the ferrocyanide is very small, and the potential is large. As soon as the zinc ions are quantitatively precipitated, however, the next drop of ferrocyanide solution causes a sudden increase in $[\{Fe(CN)_6\}^{----}]$, and hence a sudden decrease in the oxidation potential. The end point may therefore be detected by any of the three indicators mentioned above. We may also titrate in the reverse manner ; the method can therefore be used for the titration of ferrocyanides by means of standard zinc solution.

In this estimation, it is essential to work, so far as possible, under uniform conditions, if concordant results are to be obtained. The titration must not be carried out too rapidly, and the solution must be thoroughly shaken throughout the titration, otherwise over-titration may easily occur. Nitrates, oxidising agents, lead, copper, cadmium, iron, manganese, nickel and cobalt must be absent.

Procedure. **Preparation of 0·05*M* potassium ferrocyanide.** Weigh out 21·12 g. of A.R. potassium ferrocyanide $K_4[Fe(CN)_6], 3H_2O$ and 0·3 g. of A.R. potassium ferricyanide, dissolve them in water, and make up to 1 litre in a volumetric flask.

If the potassium ferrocyanide is pure,

$$1 \text{ ml. } 0{\cdot}05M\ K_4[Fe(CN)_6] \equiv 0{\cdot}004904 \text{ g. Zn.}$$

Standardisation of the potassium ferrocyanide solution. Prepare a 0·1*M* zinc solution by weighing out either 1·6345 g. of A.R. zinc or 2·0345 g. of ignited A.R. zinc oxide, dissolving either in dilute sulphuric acid, and making up to 250 ml. in a volumetric flask. If exact weights are not employed, the exact concentrations may be calculated from the weights used.

Pipette 25 ml. of the zinc solution into a 250 to 350 ml. conical flask, add 50 ml. of water, 25 ml. of 7*N* sulphuric acid, 10 g. of ammonium sulphate, and several drops of diphenylbenzidine solution (Section **III, 63**)*. Titrate the cold solution slowly and with vigorous shaking until the colour change from blue-violet to pale green is permanent. Repeat the titration with two other 25 ml. portions of the zinc solution.

Calculate the volume of the potassium ferrocyanide solution equivalent to 0·01 g. of zinc, and compare this with the value deduced from the actual weight of A.R. potassium ferrocyanide used.

For further practice in this estimation, the student may determine the percentage of zinc in crystallised zinc sulphate, preferably of A.R. quality, or of zinc in commercial zinc oxide. The sample must be treated exactly as in the standardisation.

III, 146. Determination of phosphorus.—*Discussion.* The phosphorus must be in the form of orthophosphate. Upon treatment at 20° to 45°C with a large excess of ammonium molybdate solution in the presence of nitric acid, ammonium phosphomolybdate $(NH_4)_3PO_4,12MoO_3,2HNO_3;H_2O$ is precipitated; this is converted into $(NH_4)_3PO_4, 12MoO_3$ when suitably washed with dilute potassium nitrate solution.

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* If diphenylamine is used, 3 drops of the indicator are added; with more of the indicator, the results are low. The amount appears to be immaterial (up to 10 drops) for diphenylbenzidine.

The phosphorus in the washed precipitate may be determined in one of two ways.

A. It may be titrated against standard sodium hydroxide solution with phenolphthalein as indicator. The following reaction is assumed to take place :

$$(NH_4)_3PO_4,12MoO_3 + 23NaOH$$
$$= 11Na_2MoO_4 + (NH_4)_2MoO_4 + Na(NH_4)HPO_4 + 11H_2O,$$

whence 1 ml. *N* NaOH ≡ 0·001349 g. P ≡ 0·003088 g. P_2O_5.

B. The precipitate is dissolved in dilute ammonia solution, sulphuric acid added, and the resultant solution passed through a Jones reductor (the molybdenum is thus reduced to the tervalent state) into excess of ferric alum solution. The ferrous salt is titrated with standard 0·1*N* potassium permanganate.

1 Ml. *N* $KMnO_4$ ≡ 0·0008617 g. P,

since P ≡ $12MoO_3$, which is equivalent to 18 atoms or 36 equivalents of oxygen.

Procedure. Prepare the **molybdate reagent** as follows. Dissolve 100 g. of A.R. molybdic anhydride or 118 g. of A.R. molybdic acid (*ca*. 85 per cent MoO_3) in a mixture of 400 ml. of water and 80 ml. of concentrated ammonia solution ; filter, if necessary. Add the molybdate solution thus obtained slowly and with constant stirring into a solution containing 400 ml. of concentrated nitric acid and 600 ml. of water ; the end of the tube carrying the molybdate solution should dip under the surface of the dilute nitric acid. Keep the mixture in a warm place for several days, or until a portion heated to 40° to 45°C deposits no yellow precipitate. Decant the solution from any sediment, and preserve in glass-stoppered bottles.

For practice in this estimation, the student may determine the percentage of phosphorus in anhydrous sodium phosphate Na_2HPO_4, preferably of A.R. grade : this should be dried for 1 hour at 120°C and allowed to cool in a desiccator before use. Weigh out accurately 0·2 to 0·25 g. of anhydrous sodium phosphate, dissolve it in water, and dilute to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of the solution into a 250 to 350 ml. conical flask, dilute to 100 ml., and add 12 g. of pure ammonium nitrate ; shake until the solid dissolves. Add 75 ml. of the molybdate reagent, previously warmed to 40° to 45°C, slowly using a tap funnel or a drawn-out funnel, and shaking continuously. It is important not to heat above 45°C in order to avoid contamination of the precipitate with molybdic anhydride. Fit the flask with a rubber stopper, shake vigorously for 10 minutes, and allow to stand for 30 minutes. Filter the precipitate through a quantitative filter paper. Wash the flask and the precipitate with 1 per cent potassium nitrate solution until the filtrate gives no acid reaction with methyl orange ; this will require about 100 ml. of the washing liquid. Place the paper and precipitate in the original flask. Complete the determination by either of the following methods.

A. Treat the precipitate $(NH_4)_3PO_4,12MoO_3$ with a slight excess of 0·1*N* carbonate-free sodium hydroxide (say, 50 ml.). Stopper the flask and shake ; if all the precipitate does not dissolve, a further quantity of standard alkali solution must be added. Dilute to approximately 150 ml., add 5 drops of phenolphthalein indicator, and titrate with standard 0·1*N* hydrochloric acid until the pink colour is completely discharged. Complete the titration by adding standard alkali until the re-appearance of the pink colour.

Calculate the volume of standard alkali which has reacted with the precipitate, and thence the percentage of phosphorus in the original salt.

B. Dissolve the precipitate in 2*N* ammonia solution, and add excess of sulphuric acid until the concentration of the latter is about 2*N*. Pass the solution at once through a Jones reductor (Section **III, 51B**) into 50 ml. of A.R. ferric alum solution (100 g. of A.R. crystals, and 25 ml. each of concentrated sulphuric acid and syrupy phosphoric acid in 1 litre). Wash with about 200 ml. of water, and titrate the ferrous salt with standard 0·1*N* potassium permanganate. Carry out a blank on the acid, water, and ferric alum solution.

Calculate the percentage of phosphorus in the original solid.

III, 147. Determination of temporary and permanent hardness of water.—*Discussion*. Waters are described as " soft " or " hard " according to their action upon soap. A water is said to be " soft " if it gives an immediate lather with soap solution, and " hard " if a lather is obtained with difficulty. Hardness is due almost entirely to the presence of calcium and magnesium ions ; these combine with the anions of the soap (usually sodium or potassium salts of oleic, palmitic or stearic acids) to form insoluble calcium and magnesium compounds. The actual salts present in hard water are the bicarbonates, chlorides, and sulphates of calcium and magnesium, Upon boiling hard water, the bicarbonates are decomposed with the precipitation of the normal carbonates :

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The hardness due to the presence of alkaline-earth bicarbonates therefore largely disappears on boiling (a little of the resultant carbonate dissolves in the water) ; this hardness is designated as **temporary hardness.** The residual hardness, due to the chlorides and sulphates of the alkaline earths and the amount of their carbonates soluble in pure water, cannot be removed by boiling and is termed **permanent hardness.** The sum of the temporary and permanent hardness of a water represents the **total hardness.**

The most accurate method for the estimation of the total hardness is to determine the calcium and magnesium by a gravimetric procedure ; the result is expressed in terms of calcium carbonate. Two other procedures, Clark's and the titration method, are in general use, but these do not give identical results. Clark's method is the older process ; accurate results are not obtained if a large quantity of magnesium salts is present, but this is rarely the case in actual practice. It has the advantage, however, that it does measure the soap-consuming power of the water. The titration method gives better results on the whole, since magnesium salts are quantitatively precipitated when it is used.

Hardness is conveniently expressed as parts of $CaCO_3$ per 100,000 parts of water ; if a solution contains *n* parts of $CaCO_3$ in 100,000 parts of water, it possesses ***n* degrees of hardness.** This is the standard employed in France, and will be adopted in this book. In Germany, each degree of hardness indicates 1 part of CaO in 100,000 parts of water. The term " English degree of hardness " is sometimes applied to the hardness based upon grains of $CaCO_3$ per gallon of water (1 Imperial gallon = 70,000 grains). In the United States, hardness is given in terms of grains of $CaCO_3$ per U.S. gallon, which is five-sixths as large as the Imperial gallon. Hence : 1 " French " degree = 0·56 " German " degree = 0·70 " English " degree = 0·585 " U.S." degree. When magnesium salts are present, they are expressed in terms of the equivalent amounts of $CaCO_3$ or of CaO.

Procedure A. **Clark's method.** This method must be carried out with care and slowly, especially for waters containing magnesium salts ; the experimental conditions must be closely followed. Before commencing the determination, it is advisable to estimate the total solid matter present by evaporating a known volume of the water, and weighing the residue. This gives a useful *approximate* idea as to how much to use for the soap test. The total hardness for many waters is about one half the total solids, and the sample may be so diluted, if necessary, as to bring it within the limits mentioned below. Thus if a water contains 50 grains of solids per gallon (*i.e.*, *ca.* 70 parts per 100,000), take 25 ml. for hardness.

The tedious and time-consuming evaporation of a known volume of water can be avoided by employing the volumetric trial and error method. Thus determine whether 50 ml. of the water will produce a lather with 15 ml. of standard soap solution (details are given below) ; if no lather is produced, try 20 ml. of the soap solution, and continue the process until the approximate volume of soap solution required to produce a permanent lather is ascertained.

Preparation of standard solution of calcium chloride. Weigh out accurately 0·2000 g. of pure calcite (or of A.R. calcium carbonate) and dissolve it in dilute hydrochloric acid, taking care to keep the vessel covered with a clock glass to prevent loss by spirting. Use a platinum dish if available, otherwise employ a Pyrex vessel. When all the solid has dissolved, evaporate to dryness on the water bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of the free acid. Finally, dissolve the residue of calcium chloride in distilled water, and make up to 1 litre in a standard flask.

50 Ml. of this solution correspond to 10 mg. of $CaCO_3$.

Preparation of standard solution of soap. *Method* 1. Weigh out 10 g. of soft soap (*Sapo molles*, B.P.)*, and dissolve it in 1 litre of a mixture of equal volumes of industrial methylated spirit and distilled water.

Method 2. Weigh out 50 g. of oleic acid into a beaker, and add 100 ml. of alcoholic potash, made by dissolving 20 g. of potassium hydroxide (sticks or pellets) in 180 ml. of industrial spirit ; continue adding the same solution from a burette until a drop of the oleate just gives a red colour with phenolphthalein spotted on a white plate—about 10 ml. more being required. Make the volume up to 500 ml. by the addition of the methylated spirit. 56·25 Ml. of the solution thus obtained are diluted with a mixture of industrial methylated spirit (2 vols.) and water (1 vol.) to 1 litre.

* For elementary work, the so-called " Castile " soap is satisfactory.

In either case, the solution is set aside in a cool place (preferably in an ice chest) for 24 hours, filtered through a double filter, and standardised against the standard calcium chloride solution as described below. The soap solutions will be a little too concentrated, and are to be diluted to such strength that exactly 14·25 ml. are required to form a permanent lather with 50 ml. of the calcium chloride solution.

Standardisation of the soap solution. Measure out 50 ml. of the standard calcium chloride solution into a glass-stoppered bottle of about 250 ml. capacity. Run in 1 ml. of the soap solution from a burette into the bottle, close the bottle, and shake it vigorously for a short time. If no permanent lather is formed, add another 1 ml., and shake again. Continue the addition of the soap solution, shaking the mixture well after each addition, until a lather is produced which remains for a short time when the bottle is laid upon the bench. The titration is complete when the lather remains upon the surface in an unbroken layer for 5 minutes even when the bottle is rolled half-way round on its side. Towards the end of the titration, the volume of soap solution which is added each time should be decreased, and it should finally not exceed 0·2 to 0·3 ml. Repeat the titration with another 50 ml. of the standard calcium chloride solution ; add the soap solution 1 ml. (or less) at a time, with shaking after each addition, and never in large quantities.

Dilute the soap solution with the calculated volume of the water-methylated spirit mixture such that exactly 14·25 ml. of the final solution are required to produce a lather with 50 ml. of the standard calcium chloride solution.

Determination of the total hardness. Measure out 50 ml. of the water, or, if necessary, a smaller quantity* (usually 25 ml. or 10 ml., together with 25 ml. or 40 ml. of recently boiled and cooled distilled water) into a 250 ml. glass-stoppered bottle. Titrate the water with the soap solution as described under the standardisation. Waters containing much magnesium salts give a false or " ghost " lather after the addition of only a few ml. of soap solution ; this, however, disappears entirely on allowing the bottle to remain for several minutes on its side after an extra vigorous shaking. Such water must always be diluted so that not more than 7 ml. of soap solution are required to produce a permanent lather. Repeat the titration.

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* A titre of less than 16 ml. of the soap solution should be obtained. The requisite volume of the water is obtained either from an estimation of the total solids or by a preliminary titration with 50 ml. of the water.

Ascertain the hardness from Table XXIV; multiply the result by 2 or 5 when 25 ml. or 10 ml. of the water, diluted to 50 ml., have been used. It should be pointed out that some authors prefer to regard the actual titre as the real measure of the hardness, and consider the Table of little significance for finding the true amount of $CaCO_3$.

TABLE XXIV. TABLE OF HARDNESS, PARTS IN 100,000.
(Calculated for titrations of 50 ml. of water.)

Ml. of soap solution	*$CaCO_3$ per 100,000*	*Ml. of soap solution*	*$CaCO_3$ per 100,000*	*Ml. of soap solution*	*$CaCO_3$ per 100,000*	*Ml. of soap solution*	*$CaCO_3$ per 100,000*
—	—	4·0	4·57	8·0	10·30	12·0	16·43
—	—	4·1	4·71	8·1	10·45	12·1	16·39
—	—	4·2	4·86	8·2	10·60	12·2	16·75
—	—	4·3	5·00	8·3	10·75	12·3	16·90
—	—	4·4	5·14	8·4	10·90	12·4	17·06
—	—	4·5	5·29	8·5	11·05	12·5	17·22
—	—	4·6	5·43	8·6	11·20	12·6	17·38
0·7	0·00	4·7	5·57	8·7	11·35	12·7	17·54
0·8	0·16	4·8	5·71	8·8	11·50	12·8	17·70
0·9	0·32	4·9	5·86	8·9	11·65	12·9	17·86
1·0	0·48	5·0	6·00	9·0	11·80	13·0	18·02
1·1	0·63	5·1	6·14	9·1	11·95	13·1	18·17
1·2	0·79	5·2	6·29	9·2	12·11	13·2	18·33
1·3	0·95	5·3	6·43	9·3	12·26	13·3	18·49
1·4	1·11	5·4	6·57	9·4	12·41	13·4	18·65
1·5	1·27	5·5	6·71	9·5	12·56	13·5	18·81
1·6	1·43	5·6	6·86	9·6	12·71	13·6	18·97
1·7	1·56	5·7	7·00	9·7	12·86	13·7	19·13
1·8	1·69	5·8	7·14	9·8	13·01	13·8	19·29
1·9	1·82	5·9	7·29	9·9	13·16	13·9	19·44
2·0	1·95	6·0	7·43	10·0	13·31	14·0	19·60
2·1	2·08	6·1	7·57	10·1	13·46	14·1	19·76
2·2	2·21	6·2	7·71	10·2	13·61	14·2	19·92
2·3	2·34	6·3	7·86	10·3	13·76	14·3	20·08
2·4	2·47	6·4	8·00	10·4	13·91	14·4	20·24
2·5	2·60	6·5	8·14	10·5	14·06	14·5	20·40
2·6	2·73	6·6	8·29	10·6	14·21	14·6	20·56
2·7	2·86	6·7	8·43	10·7	14·37	14·7	20·71
2·8	2·99	6·8	8·57	10·8	14·52	14·8	20·87
2·9	3·12	6·9	8·71	10·9	14·68	14·9	21·03
3·0	3·25	7·0	8·86	11·0	14·84	15·0	21·19
3·1	3·38	7·1	9·00	11·1	15·00	15·1	21·35
3·2	3·51	7·2	9·14	11·2	15·16	15·2	21·51
3·3	3·64	7·3	9·29	11·3	15·32	15·3	21·68
3·4	3·77	7·4	9·43	11·4	15·48	15·4	21·85
3·5	3·90	7·5	9·57	11·5	15·63	15·5	22·02
3·6	4·03	7·6	9·71	11·6	15·79	15·6	22·18
3·7	4·16	7·7	9·86	11·7	15·95	15·7	22·35
3·8	4·29	7·8	10·00	11·8	16·11	15·8	22·52
3·9	4·43	7·9	10·15	11·9	16·27	15·9	22·69
—	—	—	—	—	—	16·0	22·86

Determination of permanent hardness. Boil a known volume (say, 100 ml.) of the water gently in an open flask for 30 minutes. Mark the original level of the water in the flask, and add hot distilled water from time to time to make up the loss by evaporation. At the end of 30 minutes, cover the flask loosely and cool to the laboratory temperature, then make up to the original volume by the addition of recently boiled and cooled distilled water. Filter through a dry filter, and determine the hardness in the filtrate by titration with standard soap solution.

Determination of temporary hardness. The difference between the total hardness and the permanent hardness gives the temporary hardness of the water.

Procedure B. **Titration method.** Place 500 ml. of the water, or a smaller volume (250 or 100 ml.) if the water is very hard, into a large evaporating dish or casserole, add a few drops of methyl orange or, preferably, methyl orange-indigo carmine indicator, and add standard $0{\cdot}1N$ hydrochloric acid from a burette until the end point is reached. It is advisable to add the same amount of indicator to 500 ml. of distilled water and introduce the standard acid until the "acid" colour is produced. The tint can then be matched by that of the water under examination ; the blank correction is also determined at the same time. Subtract the blank correction from the volume of standard acid used, and thence calculate the corresponding weight of $CaCO_3$ and convert it into parts per 100,000.

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2H_2O + 2CO_2,$$
$$i.e., \quad 1 \text{ ml. } 0{\cdot}1N \text{ HCl} \equiv 0{\cdot}005005 \text{ g. } CaCo_3.$$

Note. The number of ml. of acid used is often regarded as the temporary hardness. This, however, includes some calcium carbonate which would remain in solution after boiling, and it is better to term it the **alkalinity.** An empirical deduction of 0·4 ml. for $0{\cdot}1N$ acid is then made to allow for the solubility of the calcium carbonate, and the difference represents **temporary hardness.**

Determination of permanent hardness. Measure out 250 ml. of the water into a conical flask, best of Pyrex glass, and boil for 30 minutes. Add an excess (say, 50 ml.) of standard $0{\cdot}1N$ sodium carbonate, and evaporate to dryness on the water bath. Take up the residue in a little boiled-out distilled water, filter through a dry quantitative filter paper, and wash the residue four times with hot water. Allow the filtrate to cool, and make it up to 250 ml. in a volumetric flask with boiled-out distilled water. Titrate 50 ml. or 100 ml. with standard 0·1*N* hydrochloric acid, using methyl orange or better, methyl orange-indigo carmine indicator.

Calculate the volume of residual 0·1*N* sodium carbonate, and from this the volume of 0·1*N* sodium carbonate consumed in precipitating the alkaline earth salts of the strong acids.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4\,;$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl.$$
$$1 \text{ Ml. } 0{\cdot}1N\ Na_2CO_3 \equiv 0{\cdot}005005 \text{ g. } CaCO_3.$$

Calculate the permanent hardness of the water (parts of $CaCO_3$ per 100,000).

III, 148. Determination of sodium.—The sodium is precipitated as $NaZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$ or as $NaMg(UO_2)_3(C_2H_3O_2)_9$, $6{\cdot}5H_2O$ (Section **IV, 47B** and **C**), and the uranium determined according to Section **III, 91.**

III, 149. Determination of potassium.—The potassium is precipitated as $K_2Na[Co(NO_2)_6]$ (Section **IV, 48C**), and the nitrite in the precipitate determined with ceric sulphate (Section **III, 79**).

III, 150. Determination of cadmium.—The cadmium is precipitated as the β-naphthaquinoline complex $[(C_{13}H_9N)_2H_2]CdI_4$ (Section **IV, 18B**). The precipitate is decomposed with *ca.* 20 ml. of 2*N* ammonium or sodium hydroxide, and the solution treated successively with 60 ml. of 2*N* hydrochloric or sulphuric acid, 5 ml. of 10 per cent potassium cyanide solution, and 2 ml. of starch solution. The mixture is then titrated with 0·025*M* potassium iodate (Section **III, 123**) until the starch is completely decolourised.

$$1 \text{ Ml. } 0{\cdot}025M\ KIO_3 \equiv 0{\cdot}001405 \text{ g. Cd.}$$

CHAPTER IV

GRAVIMETRIC ANALYSIS

IV, I. General discussion.—Before commencing experimental work in gravimetric analysis, the student should be familiar with the general theory underlying the chief experimental processes outlined in Sections **I, 54** to **I, 71**. He should also read the account of the technique of gravimetric analysis given in Sections **II, 26** to **II, 36** ; this will assume a greater significance when the various processes have actually been employed in practice. It is proposed, in the first place, to give an account of a number of typical gravimetric determinations. These estimations may be performed with substances which are readily obtainable in a state of purity (*e.g.*, of analytical reagent quality), and the experimental error can therefore be checked by calculation. Many may, however, prefer to carry out the analyses with solutions or solids of " unknown " composition. A list of solutions and of solids which are suitable for this purpose is given in the Appendix, Section **A, 7.** These determinations should be carried out before those described under the heading of SYSTEMATIC GRAVIMETRIC ANALYSIS are attempted. In general, the experimental procedures will not be given in such detail in the latter.

IV, II. Note-book, entries, and calculations.—A note-book of not less than quarto size and provided with stout cardboard covers will be found suitable for the entry of results. The right-hand page should contain the nature of the determination, the date when it was commenced (and, if desired, completed), a description in the past tense of the experimental details of the estimation, together with any relevant equations. The actual experimental results (weights, etc.), should be entered on the left-hand page ; essential details of the calculations should also be recorded here. Finally, a line or two should be devoted to the main results of the analysis.

Experimental results should on no account be entered on scraps of paper, for these are readily lost.

IV, 3. Calculations of gravimetric analysis. Chemical factors.—The calculation of the weight of a constituent in a given precipitate follows directly from the proportion :

$$M_nA_p : nM :: w : x,$$

where M_nA_p is the molecular weight of the precipitate, M the atomic (or molecular) weight of the element (or radical) sought, n the number of atomic (or molecular) weights of M in the molecular weight M_nA_p, w is the weight of precipitate, and x is the weight of the constituent desired. Furthermore, if W is the weight of the sample used, the percentage of the constituent sought y is given by :

$$x : W :: y : 100,$$

$$\text{or} \qquad y = x \times 100/W.$$

Example. 1·000 Gram of an iron compound, after suitable treatment, yielded 0·1565 g. of ferric oxide. Calculate the percentage of iron in the compound.

$$Fe_2O_3 \quad : \quad 2Fe \quad :: \quad 0{\cdot}1565 \quad : \quad x$$

$$159{\cdot}68 \quad : \quad 2 \times 55{\cdot}84 \quad :: \quad 0{\cdot}1565 \quad : \quad x$$

(Mol. wt. of Fe_2O_3) (2 × At. Wt. of Fe)

$$x = \frac{111{\cdot}68}{159{\cdot}68} \times 0{\cdot}1565 = 0{\cdot}6994 \times 0{\cdot}1565$$

$$= 0{\cdot}1095 \text{ g. of Fe.}$$

Now $0{\cdot}1095 : 1{\cdot}0000 :: y : 100,$

or $y = 10{\cdot}95$ *per cent of Fe.*

Instead of evaluating proportions like the above for each determination, we can arrive at the same result by one multiplication if we multiply the weight of the precipitate by that number which represents the weight of the constituent corresponding to 1 g. of precipitate. Such a number is called a **chemical factor.** For example, the factor for Fe in Fe_2O_3 is 0·6994, and if, in the above example, we multiply 0·1565 by this number, we obtain 0·1095, which is the same result as is obtained by evaluating the proportion.

A Table of important chemical conversion factors, together with their logarithms, is given in the Appendix, Section **A, 2.**

SIMPLE GRAVIMETRIC DETERMINATIONS

IV, 4. Determination of water of hydration in crystallised barium chloride.—*Discussion.* Barium chloride dihydrate loses all its water of crystallisation above 100°C. Much higher temperatures can be used in this dehydration, for anhydrous barium chloride is non-volatile and stable even at fairly high temperatures.

$$BaCl_2,2H_2O = BaCl_2 + 2H_2O.$$

With some hydrated salts, special temperature limits must be observed.

Procedure. Heat a crucible and lid to dull redness for several minutes, allow to cool in a desiccator, and weigh after 30 minutes. Introduce into the crucible 1 to 1·5 g. of A.R. barium chloride, and weigh again. Place the covered crucible, resting upon a pipe-clay or silica triangle, about 15 cm. above a small flame (not more than 5 to 6 cm. high). At intervals of a few minutes increase the flame gradually until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about 10 minutes, allow it to cool in a desiccator for 30 minutes, and weigh. Repeat the process until constant weight (two consecutive weighings agreeing within 0·0002 g.) is obtained.

From the loss in weight, calculate the percentage of water in barium chloride dihydrate.

A number of determinations may be carried out by simple ignition. These include iron in ferric ammonium alum ($(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O \rightarrow Fe_2O_3$), aluminium in ammonium alum ($(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O \rightarrow Al_2O_3$), bismuth in bismuth oxynitrate and carbonate (residue is Bi_2O_3), and zinc in basic zinc carbonate (residue is ZnO). The conversion factors (see Appendix, Section **A, 2**) must, of course, be known.

Note. Similar estimations may be carried out with magnesium sulphate heptahydrate ($MgSO_4, 7H_2O = MgSO_4 + 7H_2O$), borax or disodium pyroborate decahydrate ($Na_2B_4O_7, 10H_2O = Na_2B_4O_7 + 10H_2O$), and with disodium hydrogen phosphate dodecahydrate ($2Na_2HPO_4, 12H_2O = Na_4P_2O_7 + 25H_2O$).

IV, 5. Determination of chloride as silver chloride.—*Discussion.* The aqueous solution of the chloride is acidified with dilute nitric acid in order to prevent the precipitation of other silver salts, such as the phosphate and carbonate, which might form in neutral solution, and also to produce a more readily filterable precipitate. A slight excess of silver nitrate solution is added when silver chloride is precipitated :

$$Cl^- + Ag^+ \rightarrow AgCl.$$

The precipitate, which is initially colloidal, is coagulated into curds by heating the solution and stirring the suspension vigorously ; the supernatant liquid becomes almost clear. The precipitate is collected in a filter crucible, washed with very dilute nitric acid, in order to prevent it from becoming colloidal (Section **I, 36**), dried at 130° to 150°C, and finally weighed as AgCl. If a quantitative filter paper is used for filtration (Section **II, 28**), a procedure which is not recommended, the filter paper is finally washed with a little water to remove acid, which would attack the paper when dried. The paper and precipitate is dried at 100°C, and the paper is burnt separately (Section **II, 36C**) ; the ash is treated with a little nitric acid and a drop or two of concentrated hydrochloric acid, and evaporated on the water bath to convert the reduced silver back to silver chloride. The main precipitate is then added to the crucible, and the whole dried at 130° to 150°C.

Silver chloride has a solubility in water of 1·5 mg. per litre at 21°C and 21·7 mg. per litre at 100°C. The solubility is less in the presence of very dilute nitric acid (up to 1 per cent), and is very much less in the presence of moderate concentrations of silver nitrate (see Section **I, 8** ; the optimum concentration of silver nitrate is 0·05 g. per litre, but the solubility is negligibly small up to about 1·7 g. per litre). Under the conditions of the precipitation, very little occlusion occurs. If silver chloride is washed with pure water, it may become colloidal and run through the filter. For this reason the wash solution should contain an electrolyte (compare Section **I, 56**). Nitric acid is generally employed because it is without action on the precipitate and is readily volatile ; its concentration need not be greater than 0·01*N*. Completeness of washing of the precipitate is tested for by determining whether the excess of the precipitating agent, silver nitrate, has been removed. This may be done by adding 1 or 2 drops of 0·1*N* hydrochloric acid to 3 to 5 ml. of the washings collected after the washing process has been continued for some time ; if the solution remains clear or exhibits only a very slight opalescence, all the silver nitrate has been removed.

Silver chloride is light sensitive. Decomposition is only slight in diffused light, but is considerable in bright light. Hence the determination must be carried out in as subdued a light as possible, and when the solution containing the precipitate is set aside, it should be placed in the dark (*e.g.*, in a locker) or the vessel containing it should be covered with thick brown paper.

Procedure. Weigh out accurately about 0·2 g. (or an amount containing approximately 0·1 g. of chlorine) * into a 250 to 350 ml. beaker provided with a stirring rod and covered with a clock glass. Add about 150 ml. of water, stir until the solid has dissolved, and add 0·5 ml. of concentrated nitric acid. To the cold solution, add 0·1*N* silver nitrate slowly and with constant stirring. Only a slight excess should be added; this is readily detected by allowing the precipitate to settle and adding a few drops of silver nitrate solution, when no further precipitate should be obtained. *Carry out the determination in subdued light.* Heat the suspension nearly to boiling, while stirring constantly, and maintain it at this temperature until the precipitate coagulates and the supernatant liquid is clear (2 to 3 minutes). Make certain that precipitation is complete by adding a few drops of silver nitrate solution to the supernatant liquid. If no further precipitate appears, set the beaker aside in the dark, and allow the solution to stand for at least 1 to 2 hours before filtration. In the meantime prepare a filter crucible (Gooch, porous porcelain or sintered glass; the last-named is most convenient); the crucible must be dried at the same temperature as is employed in heating the precipitate (130° to 150°C) and allowed to cool in a desiccator (see Sections **II, 31, 33** for details). Collect the precipitate in the weighed filter crucible (Section **II, 35**). Wash the precipitate 2 or 3 times by decantation with cold 0·01 to 0·02*N* nitric acid before transferring the precipitate to the crucible. Remove the last small particles of silver chloride adhering to the beaker with a " policeman " (Section **II, 10L**). Wash the precipitate in the crucible with 0·01 to 0·02*N* nitric acid added in small portions (see Sections **I, 60** and **II, 34**) until 3 to 5 ml. of the washings, collected in a test-tube, give no turbidity with 1 or 2 drops of 0·1*N* hydrochloric acid.* Place the crucible and contents in an air oven at 130° to 150°C for 1 hour, allow to cool in a desiccator, and weigh. Repeat the heating and cooling until constant weight is attained.

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* A.R. Potassium or sodium chloride is suitable.

Calculate the percentage of chlorine in the sample.† The factor for converting silver chloride to chlorine is 0·24737.

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* A rapid method for weighing the silver chloride, collected in a porous porcelain or sintered glass crucible, is as follows (J. Dick, 1929). (This method should *not* be used by elementary students or beginners in the study of quantitative analysis.) After washing the precipitate with very dilute nitric acid, wash the walls of the crucible 5 or 6 times with small volumes of rectified spirit (a small pipette or a drawn-out glass tube is useful for this purpose), followed by several times with small volumes of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible with a clean linen cloth, leave in a vacuum desiccator for 10 minutes, and weigh as AgCl. The procedure may be employed for silver bromide, iodide, and thiocyanate.

† In this and all other gravimetric determinations, duplicate estimations are advisable. Both determinations may be carried out simultaneously, or if this is not convenient, the second should be commenced as soon as possible after the first is in progress.

Note on the gravimetric standardisation of hydrochloric acid. The gravimetric standardisation of hydrochloric acid by precipitation as silver chloride is a convenient and accurate method, which has the additional advantage of being independent of the purity of any primary standard (compare Section **III, 4**). Measure out from a burette 30 to 40 ml. of the, say, $0{\cdot}1N$ hydrochloric acid which is to be standardised. Dilute to 150 ml., precipitate (but omit the addition of nitric acid), filter, and weigh the silver chloride. From the weight of the precipitate, calculate the chloride concentration of the solution, and thence the normality of the hydrochloric acid.

IV, 6. Determination of sulphate as barium sulphate.—*Discussion.* The method consists in slowly adding a dilute solution of barium chloride to a hot solution of the sulphate slightly acidified with hydrochloric acid :

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4.$$

The precipitate is filtered off, washed with water, carefully ignited at a red heat, and weighed as barium sulphate. The percentage of sulphate is calculated from the weight of barium sulphate.

The reaction appears to be a simple one, but is in reality subject to numerous possible errors ; satisfactory results can only be obtained if the experimental conditions are carefully controlled. Before some of these are discussed, the student is recommended to read Sections **I, 56** to **I, 59.**

Barium sulphate has a solubility in water of about 3 mg. per litre at the ordinary temperature. The solubility is increased in the presence of mineral acids, because of the formation of the bisulphate ion ($SO_4^{--} + H^+ \rightleftharpoons HSO_4^-$) ; thus the solubilities at room temperature in the presence of 0·1, 0·5, 1·0 and $2{\cdot}0N$ hydrochloric acid are 10, 47, 87 and 101 mg. per litre respectively; but the solubility is less in the presence of a moderate excess of barium ions. Nevertheless, it is customary to carry out the precipitation in weakly acid solution in order to prevent the possible formation of the barium salts of, such anions as chromate, carbonate, and phosphate, which are insoluble in neutral solutions ; moreover, the precipitate thus obtained consists of large crystals and is therefore more easily filtered (compare Section **I, 57**). It is also of great importance to carry out the precipitation at boiling temperature, for the relative supersaturation is less at higher temperatures (compare Section **I, 57**). The concentration of hydrochloric acid is, of course, limited by the solubility of the barium sulphate, but it has been found that a concentration of $0{\cdot}05N$ is suitable ; the solubility of the precipitate in the presence of barium chloride at this acidity is negligible. The precipitate may be washed with cold water, and losses, owing to solubility influences, may be neglected except for the most accurate work.

Barium sulphate exhibits a remarkable tendency to carry down other salts (see coprecipitation, Section **I, 58**). Whether the results will be low or high will depend upon the nature of the coprecipitated salt. Thus barium chloride and barium nitrate are readily coprecipitated. These salts will be an addition to the true weight of the barium sulphate, hence the results will be high, since the chloride is unchanged upon ignition and the nitrate will yield barium oxide. The error due to the chloride will be considerably reduced by the very slow addition of hot dilute barium chloride solution to the hot solution, which is constantly stirred ; that due to the nitrate cannot be avoided, and hence nitrate ion must always be removed by evaporation with a large excess of hydrochloric acid before precipitation. Chlorate has a similar effect to nitrate, and is similarly removed.

In the presence of certain cations (sodium, potassium, lithium, calcium, aluminium, chromium, and ferric iron), coprecipitation of the sulphates of these metals occurs, and the results will accordingly be low. This error cannot be entirely avoided except by the removal of the interfering ions. Aluminium, chromium and iron may be removed by precipitation, and the influence of the other ions, if present, is reduced by considerably diluting the solution and by digesting the precipitate (Section **I, 58**). It must be pointed out that the general method of reprecipitation cannot be employed in order to obtain a purer precipitate, because no simple solvent (other than concentrated sulphuric acid) is available in which the precipitate may be dissolved.

Pure barium sulphate is not decomposed when heated in dry air until a temperature of about 1400°C :

$$BaSO_4 \rightarrow BaO + SO_3.$$

The precipitate is, however, easily reduced to sulphide at temperatures above 600°C by the carbon of the filter paper :

$$BaSO_4 + 4C = BaS + 4CO.$$

The reduction is avoided by first charring the paper without inflaming, and then burning off the carbon slowly at a low temperature with free access of air. If a reduced precipitate is obtained, it may be re-oxidised by treatment with sulphuric acid, followed by volatilisation of the acid and reheating.

The final ignition of the barium sulphate need not be made at a higher temperature than 600° to 800°C (dull red heat). A silica Gooch crucible or a Jena quartz filter crucible may be used, and the difficulty of reduction by carbon is entirely avoided.

Procedure. Weigh out accurately about 0·5 g. of the solid* (or a sufficient amount to contain 0·05 to 0·1 g. of sulphur) into a 400 ml. beaker, provided with a stirring rod and clock-glass cover. Dissolve the solid in about 25 ml. of water, add 0·5 to 1 ml. of concentrated hydrochloric acid, and dilute to 250 to 300 ml. Heat the solution to boiling, add dropwise from a burette or pipette 20 ml. of 5 per cent barium chloride solution (5 g. $BaCl_2,2H_2O$ in 100 ml. of water—*ca.* $2M$). Stir the solution constantly during the addition. Allow the precipitate to settle for a minute or two, stirring meanwhile, and test the supernatant liquid for complete precipitation by adding a few drops of barium chloride solution. If a precipitate is formed, add slowly a further 5 ml. of the reagent, and test again ; repeat this operation until an excess of barium chloride is present. When an excess of the precipitating agent has been added, keep the covered solution hot, but not boiling, for an hour (steam bath, low temperature hot plate, or small flame) in order to allow time for complete precipitation.† The volume of the solution should not be allowed to fall below 200 ml. ; if the clock glass covering the beaker is removed, the under side must be rinsed off into the beaker by means of a stream of water from a wash bottle. The precipitate should settle readily and a clear supernatant liquid should be obtained. Test the latter with a few drops of barium chloride solution for complete precipitation. If no precipitate is obtained, the barium sulphate is ready for filtration. The determination may be completed by either of the following processes.

(i) **Filter paper method.** Decant the clear solution through an ashless filter paper (Whatman, No. 40 or No. 540) (Section **II, 28**), and collect the filtrate in a clean beaker. Test the filtrate with a few drops of barium chloride : if a precipitate forms, the entire sample must be discarded and a new determination commenced. If no precipitate forms, discard the liquid, rinse out the beaker, and place it under the funnel ; this is in order to avoid the necessity of refiltering the whole solution if any precipitate should pass through the filter. Transfer the precipitate to the filter with the aid of a jet of hot water from the wash bottle (Section **II, 35**). Use a " policeman " to remove any precipitate adhering to the walls of the beaker or to the stirring rod, and transfer the precipitate to the filter paper. Wash the precipitate with small portions of hot water. Direct the jet as near the top of the filter paper as possible, and let each portion of the wash solution run through before adding the next (Section **II, 34**). Continue the washing until about 5 ml. of the wash solution gives no opalescence with a drop or two of silver nitrate solution. Eight or ten washings are usually necessary.

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* A.R. Potassium sulphate may be employed.

† An equivalent result is obtained by allowing the solution to stand at the ordinary temperature for about 18 hours.

Fold the moist paper around the precipitate and place it in a weighed porcelain crucible, previously ignited to redness and cooled in a desiccator. Dry the paper by placing the loosely-covered crucible upon a triangle several cms. above a small flame (Section **II, 36**). Then gradually increase the heat until the paper chars and volatile matter is expelled. Do not allow the paper to burst into flame as mechanical loss may thus ensue. When the charring is complete, raise the temperature of the crucible to dull redness, and burn off the carbon with free access of air* (crucible slightly inclined with cover displaced, Fig. 2-37). When the precipitate is white, ignite the crucible at a red heat for 10 to 15 minutes. Then allow the crucible to cool somewhat in the air, transfer it to a desiccator, and, when cold, weigh the crucible and contents. Repeat the ignition with 10 minute periods of heating, subsequent cooling in a desiccator, etc., until constant weight (± 0·0002 g.) is attained.

Calculate the percentage of SO_4 in the sample. The factor for converting $BaSO_4$ to S is 0·13735.

(ii) **Gooch crucible method.** Prepare a Gooch crucible as described in Section **II, 31.** A silica Gooch crucible is preferable to one of porcelain ; alternatively a Jena quartz filter crucible (Section **II, 33**) may be used, and no preliminary preparation, apart from drying at the correct temperature, is necessary. Ignite this inside a porcelain or nickel crucible (Fig. 2-33) at a red heat (or in an electric muffle furnace at 600° to 800°C), allow to cool in a desiccator, and weigh. Filter the supernatant liquid, after digestion of the precipitate, through the weighed crucible, using gentle suction. Reject the filtrate, after testing for complete precipitation with a little barium chloride solution. Transfer the precipitate to the crucible and wash with warm water until 5 ml. of the filtrate gives no turbidity with a few drops of silver nitrate solution. Dry the crucible and barium sulphate in an oven, and then ignite in a manner similar to that used for the empty crucible for periods of 15 minutes until constant weight is attained (1).

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* Any dark matter on the crucible cover may be removed by placing it, clean side down, on a triangle, and heating it for some time.

Note. 1. A rapid method for weighing the precipitate is as follows (J. Dick, 1929). (This procedure should *not* be employed by elementary students or beginners in the study of quantitative analysis.) Filter off the precipitated barium sulphate through a weighed crucible (Gooch, sintered glass or porous porcelain) and wash it with hot water until the chloride reaction of the washings is negative. Then wash 5 or 6 times with small volumes of rectified spirit, followed by 5 times with small volumes of anhydrous ether. Suck the precipitate dry on the pump for 10 minutes, wipe the outside of the crucible dry with a clean linen cloth, leave in a vacuum desiccator for 10 minutes (or until constant in weight), and weigh as $BaSO_4$.

Calculate the percentage of SO_4 in the sample.

IV, 7. Determination of sulphur in iron pyrites.—*Discussion.* The methods to be described apply to most insoluble sulphides. In these the sulphur is oxidised to sulphuric acid, and determined as barium sulphate. Two procedures are available for effecting the oxidation.

A. Dry Process. The oxidation is carried out by fusion with sodium peroxide, or, less efficiently, with sodium carbonate and potassium nitrate.

$$2FeS_2 + 15Na_2O_2 = Fe_2O_3 + 4Na_2SO_4 + 11Na_2O.$$

The sulphide is fused in an iron or nickel crucible with the sodium peroxide (platinum is strongly attacked—Sections **II, 16** and **II, 37**), the fused mass treated with water, filtered and acidified. The excess of peroxide is removed by boiling, and the sulphate ion precipitated with barium chloride. The decomposition of the sulphide is rapid, but the method has several disadvantages. Amongst these may be mentioned: the slight attack on the metal crucible, thus preventing the subsequent determination of the metal content of the sample; the introduction of appreciable quantities of sodium salts, thus increasing the error due to coprecipitation (Sections **I, 58** and **IV, 6**); and the danger of contamination of the sulphur from the flame gases, since sulphur dioxide is rapidly absorbed by the alkaline melt. The last error may be minimised by fitting the crucible into a hole in a sheet of asbestos or "uralite," and keeping the crucible covered during the ignition (see Section **II, 38**).

B. Wet Process. The sulphide is oxidised (i) by bromine in carbon tetrachloride solution, followed by nitric acid, (ii) by sodium chlorate and hydrochloric acid, or (iii) by a mixture of nitric and hydrochloric acids and a little bromine. The use of the last-named oxidising agent will be described ; the reaction may be represented by :

$$2FeS_2 + 6HNO_3 + 15Br_2 + 15H_2O \\ = 2Fe(NO_3)_3 + 4H_2SO_4 + 30HBr.$$

The method has the advantage of not introducing any metallic ions, but it is essential to remove the excess of nitric acid (see *Discussion* in Section **IV, 6**). The action is slower than by the fusion method.

Procedure. **A. Dry Process.** Dry some finely-powdered pyrites* at 100°C for 1 hour. Fit an iron or nickel crucible into a hole in an asbestos or " uralite " board sufficiently large to allow two-thirds of the crucible to project below the board. Place about 1 g. of A.R. anhydrous sodium carbonate into the crucible, and weigh accurately into it 0·4 to 0·5 g. of the pyrites. Add 5 to 6 g. of sodium peroxide, and mix well with a stout copper or nickel wire or with a thin glass rod. Wipe the wire or rod, if necessary, with a small piece of quantitative filter paper, and add the latter to the crucible ; cover the mixture with a thin layer of peroxide. Place the crucible in the hole in the asbestos or " uralite " sheet, and heat it with a very small flame. Increase the temperature gradually until after 10 to 15 minutes the crucible is at a *dull* red heat (the lower the temperature, the less is the crucible attacked) and just sufficient to keep the mass completely fused. Remove the cover occasionally and examine the contents ; be sure that the whole mass is fluid. Maintain the mass fluid for 15 minutes to complete the oxidation. Allow to cool, extract the crucible with water in a covered 600 ml. beaker, rinse off the crucible cover into the beaker, remove the crucible with a glass rod and wash it well ; dilute to 300 ml. Boil the solution for 15 minutes in order to destroy the excess of peroxide, add a Whatman " accelerator " or a quarter of an " ashless tablet," and filter through a Whatman No. 541 filter paper. Wash the residue at least 10 times with hot 1 per cent sodium carbonate solution. Acidify the combined filtrate and washings contained in a 800 to 1000 ml. beaker with concentrated hydrochloric acid, using methyl red or methyl orange as indicator, and add 2 ml. of acid in excess. Dilute, if necessary, to 600 ml., and heat to boiling. Precipitate the sulphuric acid by the slow addition with stirring of a boiling 5 per cent solution of barium chloride; the latter is added in slight excess of the calculated amount required, assuming the pyrites to be pure FeS_2. Complete the determination as in Section **IV, 6.**

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* Ridsdale's " Iron Pyrites, No. 28 " (one of the Analysed Samples for Students) is suitable.

Calculate the percentage of sulphur in the sample.

B. Wet process. Weigh out accurately about 0·5 g. of the finely-powdered pyrites into a 250 ml. beaker, and pour on to it a mixture of 3 volumes of concentrated nitric acid and 1 volume of concentrated hydrochloric acid to which 1 ml. of pure, sulphur-free liquid bromine (*e.g.*, A.R.) has been added. Cover the beaker with a well-fitting clock glass, let the reaction proceed at room temperature for 30 minutes, and then transfer the beaker to a steam bath. Heat gently until all the apparent action has subsided, raise the cover,* and evaporate the liquid to dryness. Treat the residue with 5 ml. of concentrated hydrochloric acid and again evaporate to dryness. Moisten the dry residue with 2 ml. of concentrated hydrochloric acid, add 100 ml. of hot water, filter into a 400 ml. beaker, and wash the residue with hot water. If the residue is small, the filtration may be omitted. To the hot filtrate, which should have a volume of 200 to 250 ml., add 1 : 1 ammonia solution slowly and with constant stirring until the solution is slightly ammoniacal, and add a further 3 to 5 ml. Filter off the ferric hydroxide (Section **IV, 8**) and wash it with hot water until free from chloride ; preserve the filtrate (*a*). Dissolve the precipitate in dilute hydrochloric acid, reprecipitate the ferric hydroxide as before, filter, and add the filtrate and washings to the one previously obtained (*a*). (This double precipitation is necessary to remove the coprecipitated sulphate ions from the ferric hydroxide.) Render the combined filtrates and washings just acid with hydrochloric acid, using methyl orange as indicator, add 2 ml. of concentrated hydrochloric acid in excess, dilute to 500 ml., and precipitate the sulphuric acid as described in the **Dry Process** above.

Calculate the percentage of sulphur in the sample.

IV, 8. Determination of iron as ferric oxide.—*Discussion.* The solution containing the ferric salt† is treated with a slight excess of ammonium hydroxide solution to precipitate ferric hydroxide* :

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* This is unnecessary if a Fisher " speedyvap " beaker cover is used.

† Ferrous iron is only partially precipitated by ammonia solution in the presence of ammonium salts.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$$

Other elements that are precipitated by ammonia solution must, of course, be absent. These include aluminium, trivalent chromium, titanium and zirconium. In the presence of an oxidising agent (even atmospheric oxygen), manganese may be precipitated as the hydrated dioxide. Anions, such as arsenate, phosphate, vanadate and silicate, which yield insoluble compounds of iron in weakly basic media, must be absent. The presence of a sufficient quantity of salts of organic hydroxy-acids (*e.g.*, citric, tartaric and salicylic acids), hydroxy compounds (*e.g.*, glycerine and sugars), alkali pyrophosphate and fluorides must be guarded against, because of the formation of complex salts and the consequent non-precipitation of ferric hydroxide.

The solubility product of ferric hydroxide is of the order of 10^{-36}, so that quantitative precipitation occurs even in weakly acid solution, and errors due to washing will be negligibly small. The precipitate first forms as a dispersed phase, but on heating in the presence of electrolytes it coagulates to a gelatinous mass, which settles out of suspension ; prolonged heating tends to break up the aggregates and causes the precipitate to become slimy. The hydrated ferric oxide is a typical example of a flocculated colloid. The coagulation of a colloidal precipitate, and especially the agglomeration of the primary particles, is aided considerably by raising the temperature of the solution. Hence precipitation is carried out at or near the boiling point, and the liquid is maintained at this temperature for a *short time* after precipitation.

As might be expected from its colloidal character, hydrated ferric oxide has a great tendency to adsorb other ions present. If precipitation is made from basic solution, the primary adsorbed ion is the hydroxyl ion (Section **I, 56**), and this readily holds by secondary adsorption positive ions which may be present. If there is a large excess of ammonium ions in the precipitating and wash solutions, the adsorption of other cations can be kept at a minimum ; since ammonium

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* The precipitate is usually given the formula $Fe(OH)_3$, ferric hydroxide. Actually the water content is somewhat indefinite ; the formula of the precipitate is more accurately represented by Fe_2O_3,xH_2O, and is termed a *hydrated oxide*. Throughout this book the terms hydrated oxide and hydroxide will be used synonymously.

$$2Fe^{+++} + 6NH_4OH + yH_2O = Fe_2O_3,xH_2O + 6NH_4^+.$$

salts are volatilised upon ignition of the precipitate, little harm is caused by the adsorption. Divalent ions are more strongly adsorbed than monovalent ions (Section **I, 58**). If the extent of coprecipitation is large, reprecipitation may be employed since the precipitate is soluble in dilute acids.

The gelatinous precipitate of ferric hydroxide is always filtered through filter paper. Filtration with suction, in order to hasten filtration, should not be used, since the effect of the suction is merely to force the small particles of the precipitate into the pores of the filtering medium. It may often happen that with suction the liquid will pass through more rapidly ; this does not mean that the washing process is accelerated since the liquid runs through small channels and does not permeate the main body of the precipitate. For this reason ferric hydroxide is best washed by decantation; the precipitate may then be thoroughly stirred with the wash liquid. To prevent peptisation and the production of slimy material, an electrolyte is used in the wash liquid. The most satisfactory is ammonium nitrate ; this volatilises upon ignition and assists somewhat in the subsequent ignition of the precipitate. Ammonium chloride is unsuitable, because ferric chloride, which is volatile, is formed during the ignition :

$$Fe_2O_3 + 6NH_4Cl = 2FeCl_3 + 6NH_3 + 3H_2O.$$

It is advisable, therefore, to wash out nearly all the ammonium chloride present in the hydrated ferric oxide : very small amounts, however, will not lead to any significant error. To assist filtration, a hot wash solution should be employed. The filtration and washing of any gelatinous precipitate is hastened by the use of ashless filter paper pulp (macerated filter paper, Section **II, 29**). Under no circumstances should the precipitate be allowed to stand in the filter paper before washing is complete, because it shrinks rapidly as it partially dries, and channels, which permit the wash liquid to run through, are formed in the precipitate.

Hydrated ferric oxide upon ignition at 1000°C yields ferric oxide ; at higher temperatures triferric tetroxide is slowly formed. The ignition should be carried out under good oxidising conditions especially during the burning of the filter paper, for otherwise partial reduction to the magnetic oxide Fe_3O_4, or even to the metal, may occur. These reduction products are only slowly converted into ferric oxide upon continued heating with free access of air. Such reduction is avoided by burning off the carbon at a low heat, by maintaining at all times free access of air, and by excluding the reducing gases from the flame.

Procedure. For practice in this determination, the student may employ either A.R. ferrous ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$ or A.R. ferric ammonium sulphate $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$.* The former is to be preferred as this estimation involves oxidation of the ferrous salt to the ferric state. Weigh out accurately about 0·8 g. of ferrous ammonium sulphate into a 400 ml. beaker provided with a clock glass and stirring rod. Dissolve it in 50 ml. of water and 10 ml. of dilute hydrochloric acid (1 : 1). Add 1 to 2 ml. of concentrated nitric acid† to the solution, and boil gently until the colour is clear yellow (3 to 5 minutes is usually necessary) (1). Dilute the solution to 200 ml.‡, heat to boiling, and slowly add pure 1 : 1 ammonia solution (2) in a slow stream from a small beaker until a slight excess is present, as is shown by the odour of the steam above the liquid (3). Boil the liquid gently for 1 minute, and allow the precipitate to settle. The supernatant liquid should be colourless. As soon as most of the precipitate has settled, decant the supernatant liquid through an ashless filter paper, but leave as much of the precipitate as possible in the beaker. It is essential that the filter paper fit the funnel properly (Section **II, 28**), so that the stem of the funnel is always filled with liquid, otherwise filtration will be very slow. Add about 100 ml. of boiling 1 per cent ammonium nitrate solution to the precipitate, stir the mixture thoroughly, and allow to settle. Decant as much liquid as possible through the filter. Wash the precipitate three to four times by decantation with 75 to 100 ml. portions of hot 1 per cent ammonium nitrate solution. Transfer the precipitate (and macerated filter paper, if employed) to the filter (Section **II, 35**) ; any small particles adhering to the sides of the vessel or to the glass rod are dislodged with the aid of a "policeman," and subsequently transferred to the main precipitate with the assistance of hot water from a wash bottle. Wash the ferric hydroxide several times with hot ammonium nitrate solution (4) until no test

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* Alternatively, the sample supplied by the teacher may be used.

† Alternatively, bromine water or hydrogen peroxide may be used for the oxidation. The latter is conveniently employed as the "100 volume" solution ; 1 ml. of this solution is sufficient. The excess of the reagent must be destroyed by boiling the solution.

‡ If iron alum is used, dissolve 1·3 g. (or a sufficient amount of a ferric salt containing about 0·15 g. of iron) in 200 ml. of water, add 10 ml. of 1 : 1 hydrochloric acid, and proceed as described.

(or, at most, a very slight test) for chloride is obtained from the washings. Allow each portion of the wash liquid to run through before adding the next portion ; do not fill the filter more than three-fourths full of the precipitate. While the filtration is in progress, ignite a clean crucible (porcelain, silica, or platinum) at a red heat, cool in a desiccator for 30 minutes, and weigh. When the filter paper has drained thoroughly, fold over the edges, and transfer to the weighed crucible (5). Proceed as described in Section **IV, 6.** Heat gradually until dry, char the paper without inflaming, and burn off the carbon as at a low a temperature as possible under good oxidising conditions. Finally, ignite the precipitate at a red heat for 15 minutes and take care to exclude the flame gases from the interior of the crucible, cool in a desiccator for 30 minutes, and weigh. Repeat the ignition (10 to 15 minutes) until constant weight is obtained (to within 0·0002 g.).

From the weight of ferric oxide obtained, calculate the percentage of iron in the salt used. The factor for converting Fe_2O_3 to Fe is 0.69940.

Notes. 1. At this stage it is advisable to test the solution for the complete oxidation of the iron. Transfer a drop of the solution to a test-tube by means of a stirring rod, and dilute with about 1 ml. of water. Add a few drops of a freshly-prepared potassium ferricyanide solution. If a blue colour appears, ferrous iron is still present in the solution, and more nitric acid must be added.

2. Filtered ammonia solution should be used in order to prevent the introduction of silica, which is often present in suspension in alkaline solutions.

3. At this point it is advantageous to add a little macerated filter paper, best in the form of a Whatman " accelerator " or " ashless tablet." For further details, see Section **II, 29.**

4. If desired, hot water from a wash bottle may be substituted at this stage ; peptisation is negligible.

5. The most convenient crucible is a silica crucible with an interior-fitting serrated lid (Main-Smith type). See Section **II, 71B.**

For other methods for the determination of iron, see Section **IV, 31.**

IV, 9. Determination of aluminium as aluminium oxide.—*Discussion.* The aluminium is precipitated as the hydrated oxide by means of ammonia solution in the presence of ammonium chloride. The gelatinous precipitate is washed, converted into the oxide by ignition, and weighed as Al_2O_3.

This determination is subject to several sources of error, most of which will now be discussed. Aluminium hydroxide is amphoteric in character :

$$Al(OH)_3 + 3H^+ \rightarrow Al^{+++} + 3H_2O ;$$
$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O.$$

Precipitation commences at approximately *p*H 4, and is complete when the *p*H lies between 6·5 and 7·5. The latter *p*H range can be maintained by the use of methyl red as indicator. The amount of ammonia solution employed for precipitation must clearly be controlled. This is achieved by the addition of ammonium chloride, which exerts a buffering effect (Section **I, 20**) and also assists the coagulation of the initially colloidal precipitate. The presence of ammonium salts reduces to a minimum the coprecipitation of the divalent metals, such as calcium and magnesium (see Section **IV, 8**) and other cations. A readily filterable precipitate is obtained by precipitation in hot solution. The precipitate cannot be washed with hot water for aluminium hydroxide is readily peptised (Section **I, 56**), and will run through the filter. A two per cent solution of either ammonium chloride or ammonium nitrate is satisfactory ; the presence of ammonium chloride in the precipitate causes no appreciable volatilisation of aluminium during the subsequent ignition (contrast ferric oxide).

The aluminium oxide obtained by igniting aluminium hydroxide is hygroscopic unless the temperature has been raised to at least 1200°C, when apparently a non-hygroscopic form of the oxide is formed. For this reason the precipitate is best ignited in a silica crucible (porcelain is slightly hygroscopic when heated to a high temperature) over a Méker or Fisher burner or with a blast lamp.

Procedure. Weigh out accurately about 1·8 g. of A.R. ammonium aluminium sulphate $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ (or a weight of a sample containing about 0·1 g. of aluminium) into a 400 or 600 ml. beaker, provided with a clock-glass cover and a stirring rod. Dissolve it in 200 ml. of water, add 5 g. of pure ammonium chloride, a few drops of methyl red indicator (0·2 per cent alcoholic solution), and heat just to boiling. Add pure dilute ammonia solution (1 : 1) dropwise from a burette until the colour of the solution changes to a distinct yellow. Boil the solution for 1 or 2 minutes, and filter at once through a suitable quantitative filter paper (Section **II, 28**) (1). Wash the precipitate thoroughly with hot 2 per cent ammonium nitrate or chloride solution. Place the paper with the precipitate in a previously ignited silica or platinum crucible (2), dry, char, and ignite for 10 to 15 minutes with a Méker or Fisher high temperature burner. Allow the crucible to cool in a desiccator, and weigh. Ignite to constant weight.

Calculate the percentage of aluminium in the sample. The factor for converting Al_2O_3 to Al is 0·52913.

Notes. 1. Macerated filter paper (Section **II, 29**) may be added in order to assist the subsequent filtration.

2. A silica crucible of the Main-Smith type (Section **II, 36B**) considerably simplifies this operation.

For other methods for the determination of aluminium, see Section **IV, 28.**

IV, 10. Determination of calcium as oxalate.—*Discussion.* The calcium is precipitated as calcium oxalate CaC_2O_4,H_2O by treating a hot hydrochloric acid solution with ammonium oxalate, and slowly neutralising with ammonium hydroxide solution :

$$Ca^{++} + C_2O_4^{--} + H_2O \rightarrow CaC_2O_4,H_2O.$$

The precipitate is washed with dilute ammonium oxalate solution and then weighed in one of the following forms :

(i) as $\mathbf{CaC_2O_4,H_2O}$ by drying at 100° to 115°C for 1 to 2 hours. This method is not recommended for accurate work, because *inter alia* of the hygroscopic nature of the oxalate and the difficulty of removing the coprecipitated ammonium oxalate at this low temperature.

(ii) As $\mathbf{CaCO_3}$ by drying at 475° to 525°C in an electric muffle furnace. This is the most satisfactory method since calcium carbonate is non-hygroscopic.

$$CaC_2O_4 = CaCO_3 + CO_2.$$

(iii) As **CaO** by igniting at 1200°C. This method is widely used, but the resultant lime has a comparatively small molecular weight and is hygroscopic ; precautions must therefore be taken to prevent absorption of moisture (and of carbon dioxide).

$$CaCO_3 + CaO + CO_2.$$

Calcium oxalate monohydrate has a solubility of 0·0067 g. and 0·0140 g. per litre at 25° and 95°C respectively. The solubility is less in neutral solutions containing moderate concentrations of ammonium oxalate owing to the common ion effect (Section **I, 9**) ; hence a dilute solution of ammonium oxalate is employed as the wash liquid in the gravimetric determination. Calcium oxalate being the salt of a weak acid, its solubility increases with increasing hydrogen ion concentration of the solution because of the removal of the oxalate ions (compare Section **I, 13**) to form the weak bi-oxalate ions and oxalic acid :

$$CaC_2O_4 \text{ (solid)} \rightleftharpoons Ca^{++} + C_2O_4^{--} ;$$

$$C_2O_4^{--} + H^+ \rightleftharpoons HC_2O_4^- ;\ HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4.$$

Calculation shows that precipitation is quantitative at a *p*H of 4 or higher.

Precipitation from cold neutral or ammoniacal solutions yields a very finely-divided precipitate, which is difficult to filter. The most satisfactory results are obtained by adding ammonium oxalate to a hot *acid* solution of the calcium salt (more or less calcium oxalate may precipitate, depending upon the *p*H of the solution), and finally neutralising with ammonium hydroxide solution. The precipitate thus obtained consists of relatively coarse crystals which are readily filtered.

In this determination all those metals (*e.g.*, copper, lead, zinc) which form slightly soluble oxalates must be absent. The problem which frequently arises in practice is the precipitation of calcium in the presence of magnesium and the alkali metals. The amount of the alkali metals which is precipitated is usually small ; in the presence of large amounts of sodium, reprecipitation may be desirable. Magnesium may be coprecipitated (Section **I, 58**) to a considerable extent, but the amount of this may be considerably reduced by not boiling the solution and not allowing the precipitate to stand in contact with the solution too long before filtration (post-precipitation, Section **I, 58**, is thus minimised). By using a very large excess of ammonium oxalate, magnesium is held in solution in the form of a complex salt with the oxalate ion ; furthermore, magnesium oxalate readily forms quite stable supersaturated solutions. If the concentration ratio of magnesium to calcium is extremely large, a second precipitation may be necessary.

As already pointed out, the two forms in which calcium oxalate is best weighed are the carbonate and oxide. The theory of the decomposition of calcium oxalate is of some interest in this connexion. Decomposition of the oxalate into the carbonate is rapid at about 475°C. At higher temperatures, the dissociation of calcium carbonate ($CaCO_3 \rightleftharpoons CaO + CO_2$) comes into play. At any given temperature, a mixture of $CaCO_3$, CaO and CO_2 in equilibrium with one another exerts a certain definite pressure of carbon dioxide. If the partial pressure of the carbon dioxide in the surrounding atmosphere is greater than the equilibrium pressure for that temperature, the above reaction will proceed from right to left, and eventually the oxide will be completely converted into the carbonate. Otherwise expressed, calcium carbonate cannot be decomposed into the oxide so long as the pressure of carbon dioxide in the surrounding atmosphere is greater than the equilibrium pressure of the system $CaCO_3$-CaO-CO_2 at the temperature of heating. Atmospheric air contains about 0·03 per cent of carbon dioxide by volume; when the pressure is 760 mm., this corresponds to $760 \times 0{\cdot}0003 = 0{\cdot}228$ mm. of mercury. Calcium carbonate will therefore be perfectly stable in the atmosphere so long as the decomposition pressure does not exceed 0·23 mm. of mercury. The dissociation pressure of calcium carbonate, expressed in mm. of mercury, at various temperatures are collected in the following table.

Temp.	*Dissociation pressure.*	*Temp.*	*Dissociation pressure.*
200°C	$7{\cdot}8 \times 10^{-9}$	700°C	31·2
400°C	$0{\cdot}3 \times 10^{-3}$	800°	208
500°	0·15	882°	760
600°	2·98	900°	984

Thus calcium carbonate will not commence to dissociate appreciably in the atmosphere until a temperature of slightly above 500°C. Actual experiment has shown that complete decomposition of calcium oxalate into the carbonate occurs at a temperature between 475° and 525°C; above 550°C the calcium carbonate commences to lose carbon dioxide. For the weighing of calcium oxalate as calcium carbonate, fine temperature control is necessary; this can only be achieved by the use of an electrically-heated muffle furnace, provided with a pyrometer or suitable thermometer. If such equipment is available, the method should be used in preference to all others; the oxalate must be filtered through a Gooch (preferably of silica) or porcelain filtering crucible and not through filter paper.

Above 882°C calcium carbonate is completely decomposed into the oxide, but unless the carbon dioxide is removed by diffusion, convection, etc., by conducting the ignition in a loosely-covered crucible, there will be a recombination of calcium oxide and carbon dioxide on cooling with the formation of some calcium carbonate. In practice it is found that the rate of decomposition at about 900°C is very slow, and it is best to use a temperature of 1100° to 1200°C. This temperature is not easily attained in a porcelain or silica crucible unless an electrically heated muffle furnace is employed.

However, quantities up to 1 g. can be completely decomposed in a platinum crucible by the use of a Méker or Fisher high temperature burner. The residue of calcium oxide is hygroscopic (unless heated for a considerable time above 1200°C). The crucible should be kept covered in a desiccator, containing pure concentrated sulphuric acid, freshly ignited quicklime, or stick sodium hydroxide, for only 25 to 30 minutes, and weighed.

Procedure. Weigh out accurately sufficient of the sample to contain 0·2 g. of calcium* into a covered 400 or 600 ml. beaker provided with a stirring rod. Add 10 ml. of water, followed by about 15 ml. of dilute hydrochloric acid (1 : 1). Heat the mixture until the solid has dissolved, and boil gently for several minutes in order to expel carbon dioxide. Rinse down the sides of the beaker and the clock glass, and dilute to 200 ml. : add 2 drops of methyl red indicator. Heat the solution to boiling, and add very slowly a warm solution of 2 g. of ammonium oxalate in 50 ml. of water. Add to the resultant solution filtered dilute ammonia solution (1 : 1) dropwise and with stirring until the mixture is neutral or faintly alkaline (colour change from red to yellow). Allow the solution to stand without further heating for at least an hour. After the precipitate has settled, test the solution with a few drops of ammonium oxalate solution for complete precipitation. The subsequent procedure will depend as to whether the calcium oxalate is to be weighed as the carbonate or as the oxide.

Weighing as calcium carbonate. Decant the clear supernatant liquid through a weighed silica Gooch crucible or a porous porcelain filtering crucible. Transfer the precipitate to the crucible with a jet of water from the wash bottle ; any precipitate adhering to the beaker or to the stirring rod is transferred with the aid of a rubber-tipped rod (" policeman "). Wash the precipitate with a cold, very dilute ammonium oxalate solution (0·1 to 0·2 per cent) at least 5 times, or until the washings give no test for chloride ion (add dilute nitric acid and a few drops of silver nitrate solution to 5 ml. of the washings). Dry the precipitate in the steam oven or at 110° to 120°C for 1 hour, and then transfer to an electrically-heated muffle furnace, maintained at 500°C, for 2 hours. Cool the crucible and contents in a desiccator, and weigh.

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* 0·5 Gram of A.R. calcium carbonate, or of calcite, which has been finely powdered in an agate mortar and dried at 110° to 130°C for 1 hour, is suitable.

Further heating at 500°C should not affect the weight. As a final precaution, moisten the precipitate with a few drops of saturated ammonium carbonate solution, dry at 110°C, and weigh again. A gain in weight indicates that some oxide was present ; this should not occur.

Calculate the percentage of calcium in the sample. The factor for converting $CaCO_3$ to Ca is 0·40044.

Weighing as calcium oxide. Decant the clear supernatant liquid through a Whatman No. 40 or 540 filter paper, transfer the precipitate to the filter (Section **II, 35**), and wash with a cold 0·1 to 0·2 per cent ammonium oxalate solution until free from chloride. Transfer the moist precipitate to a previously ignited and weighed platinum crucible, and ignite gently at first over a Bunsen flame and finally for 10 to 15 minutes with a Méker or Fisher high temperature burner until two successive weighings do not differ by more than 0·0003 g. The crucible and contents are weighed after cooling in a desiccator containing pure concentrated sulphuric acid or stick sodium hydroxide (but not calcium chloride) for 25 minutes only.

Calculate the percentage of calcium in the sample. The factor for converting CaO to Ca is 0·71469.

For other methods for the determination of calcium, see Section **IV, 43.**

IV, 11. Determination of magnesium as pyrophosphate.—*Discussion.* An acid solution of the magnesium salt is treated with an excess of diammonium hydrogen phosphate, and then excess of ammonia solution is added to precipitate magnesium ammonium phosphate at room temperature :

$$Mg^{++} + NH_4^{+} + PO_4^{---} + 6H_2O = MgNH_4PO_4,6H_2O.$$

The precipitate is washed with dilute ammonia solution,* ignited to magnesium pyrophosphate at a high temperature (1100°C), and weighed as such.

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + 2H_2O.$$

To obtain a precipitate of correct composition ($MgNH_4PO_4$) at the first precipitation is a difficult matter owing to the coprecipitation of ammonium phosphate and magnesium phosphates ; however, if the experimental conditions are carefully chosen and a pure magnesium salt is used, a precipitate of normal composition is formed. If the precipitation takes place in the presence of much ammonium salts, the precipitate contains $Mg_3(PO_4)_2$ or $Mg(NH_4)_4(PO_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate. If the precipitation is made in the presence of much potassium or sodium salts, the precipitate is contaminated with magnesium potassium (or sodium) phosphate. Hence if much ammonium, potassium or sodium salts are present, reprecipitation is essential. In any case, reprecipitation is desirable to procure the best results. The double precipitation process will accordingly be described. It is an experimental fact that the precipitate is practically insoluble in 5 per cent ammonia solution : this is accordingly used as the wash liquid.

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*Results of moderate accuracy may be obtained by weighing the precipitate as the $MgNH_4PO_4.6H_2O$. After washing on the filter crucible with dilute ammonia solution to remove soluble salts, the precipitate is washed with four 2-4 ml. portions of rectified spirit, followed by several times with small volumes of anhydrous ether. The precipitate is sucked dry at the pump for 10 minutes, the outside of the crucible wiped with a clean linen cloth, and left in a vacuum desiccator for 10-20 minutes ; the precipitate is then weighed as $MgNH_4PO_4.6H_2O$.

Great care must be taken in the conversion of magnesium ammonium phosphate into the pyrophosphate. The carbon must be burnt off at as low a temperature as possible, because of the danger of the reduction of the phosphate precipitate if the heating is strong while carbon remains ; if a platinum crucible is used, the resultant phosphorus may lead to serious injury of the crucible. Furthermore, if the heating is rapid, a dark coloured product is obtained. For these reasons, the charring of the paper and the burning off of the carbon are conducted at as low a temperature as possible ; the temperature must be raised very gradually. Some authors recommend, particularly for elementary students, that the filter paper be ignited apart from the precipitate (Section **II, 36C**) in order to minimise this danger. A porcelain filter crucible may be used to collect the precipitate ; this is then heated in an electric muffle furnace at 1050° to 1100° C.

Procedure. To a neutral or slightly acid (hydrochloric) solution of a magnesium compound, containing not more than 0·1 g. of magnesium,* add 5 ml. of concentrated hydrochloric acid, and dilute to 150 ml. Add a few drops of methyl red indicator to the cold solution, and then 10 ml. of the freshly-prepared ammonium phosphate reagent (25 g. of A.R. $(NH_4)_2HPO_4$ dissolved in 100 ml. of water). Now add pure concentrated ammonia solution slowly while stirring the solution vigorously until the indicator turns yellow. Avoid scratching the sides of the beaker with the stirring rod, for wherever there is contact, an adhering crystalline deposit forms quickly. Continue to stir the solution for 5 minutes, adding ammonia solution dropwise to keep the solution yellow, and finally add 5 ml. of concentrated ammonia solution in excess. Allow the solution to stand in a cool place for at least 4 hours or preferably overnight. Filter through a quantitative filter paper without attempting to transfer the precipitate completely, and wash the vessel, precipitate and paper several times with cold 1 : 20 ammonium hydroxide solution. Dissolve the precipitate on the paper in approximately 50 ml. of warm dilute hydrochloric acid (1 : 10), and wash the paper through with hot very dilute hydrochloric acid (1 : 100) into the beaker used for the initial precipitation, dilute to 100 to 150 ml., add a few drops of methyl red indicator, 1 ml. of the ammonium phosphate reagent, and cool to room temperature or, better, in ice. Complete the precipitation by the addition of concentrated ammonia solution dropwise and with constant stirring until the solution is yellow, and then add 5 ml. in excess. Let the solution stand for at least 4 hours or, better, overnight. Filter the precipitate through a quantitative filter paper or through a porcelain filter crucible (this time great care must be taken to clean the beaker and stirrer from adhering precipitate), and wash the precipitate with cold 1 : 20 ammonium hydroxide solution until the washings give no turbidity with dilute nitric acid and silver nitrate solution.

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* About 0·6 gram of A.R. magnesium sulphate, accurately weighed, is a convenient quantity of magnesium salt to employ for this estimation.

If a filter paper was used, fold it up, and place it in a previously ignited and weighed platinum crucible (1). Char the paper slowly without allowing it to ignite, and burn off the carbon at as low a temperature as possible with free access of air (gradually increase the flame but do not heat the crucible to more than the faintest red), and then ignite to constant weight in an electric muffle furnace at 1050° to 1100°C or, less desirably, over a Méker or Fisher high temperature burner.

If a porcelain filter crucible was used, dry it first in an air oven at 100° to 150°C and then heat it gradually to 1050° to 1100°C in an electric muffle furnace ; if an electric furnace is not available, place the porcelain crucible inside a nickel crucible (Fig. 2-33), and heat it gradually to the full heat of a Méker or equivalent burner. Heat for 25 to 30 minute periods until constant weight is attained.

Calculate the percentage of magnesium in the compound. The factor for converting $Mg_2P_2O_7$ to Mg is 0·21851.

Note. 1. For elementary students it is sufficient to dry the filter with the precipitate in the steam oven (or at 100°C), and to incinerate the filter paper apart from the precipitate (Section **II, 36C**) at as low a temperature as possible ; the paper should not be allowed to take fire. After the volatile carbonaceous matter has been burnt off, the residue may be ignited strongly with the lid of the crucible displaced, to allow circulation of the air, until the residue is as white as possible. The main precipitate is added, and the whole ignited to constant weight as described above.

For other methods for the determination of magnesium, see Section **IV, 46.**

IV, 12. Determination of nickel as the dimethylglyoxime complex.—*Discussion.* The nickel is precipitated by the addition of an alcoholic solution of dimethyglyoxime {$CH_3.C(:NOH).C(:NOH).CH_3$, referred to in what follows as H.Dmg} to a hot slightly acid solution of the nickel compound, and then adding a slight excess of ammonia solution. The precipitate is washed and weighed as nickel dimethylglyoxime after drying at 100° to 120°C (compare Section **I, 62A**) :

$$NiSO_4 + 2H.Dmg = Ni(Dmg)_2 + H_2SO_4.$$

The precipitate is soluble in free mineral acids (even as much as is liberated by reaction in neutral solution), in alcoholic solutions containing more than 50 per cent by volume, and in concentrated ammoniacal solutions of cobalt, but is insoluble in dilute ammonia solution, in solutions of ammonium salts, and in dilute acetic acid-sodium acetate solutions. Excessive amounts of ammonium hydroxide, cobalt or copper retard the precipitation. Better results are obtained in the presence of cobalt, manganese or zinc by adding sodium or ammonium acetate to precipitate the complex (compare Section **IV, 86D**) ; ferric iron must, however, be absent.

Dimethylglyoxime forms sparingly soluble salts with palladium, platinum and ferrous iron, whilst gold is reduced. These elements and indeed all the elements of the hydrogen sulphide group should be absent. Ferric iron, aluminium, and chromic chromium are rendered inactive by the addition of a soluble tartrate or citrate, with which these elements form complex ions.

Dimethyglyoxime is almost insoluble in water, and is added in the form of a 1 per cent solution in rectified spirit or absolute alcohol ; 1 ml. of this solution is sufficient for the precipitation of 0·0025 g. of nickel. As already pointed out, precipitation is made in a hot feebly acid solution of a nickel salt, and then rendering the solution faintly alkaline. This procedure gives a more easily filterable precipitate than does direct precipitation from cold or from ammoniacal solutions. Only a slight excess of the reagent should be used, since dimethylglyoxime is not very soluble in water or in very dilute alcohol and may precipitate ; if a very large excess is added (such that the alcohol content of the solution exceeds 50 per cent), some of the precipitate may dissolve.

Procedure. **A. Nickel in a nickel salt.** Weigh out accurately 0·3 to 0·4 g. of pure (preferably A.R.*) nickel ammonium sulphate $NiSO_4,(NH_4)_2SO_4,6H_2O$ into a 400 ml. beaker provided with a clock glass cover and stirring rod. Dissolve it in water, add 5 ml. of dilute hydrochloric acid (1 : 1) and dilute to 200 ml. Heat to 70° to 80°C, add a slight excess (25 to 30 ml.) of the dimethylglyoxime reagent, and immediately add dilute ammonia solution dropwise and with constant stirring until precipitation takes place and then in slight excess (alternatively, 3 to 4 g. of sodium acetate may be used to effect precipitation†). Allow to stand on the steam bath for 20 to 30 minutes, and test the solution for complete precipitation when the red precipitate has settled out. Digest on the water bath for 1 hour. Filter through a Gooch, sintered glass or porous porcelain crucible, previously heated to 110° to 120°C and weighed after cooling in a desiccator. Wash the precipitate with hot water until free from chloride, and dry it at 110° to 120°C for 45 to 60 minutes. Allow to cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Weigh as $Ni(C_4H_7O_2N_2)_2$, which contains 20·31 per cent of Ni.

Calculate the percentage of nickel in the salt.

B. Nickel in nickel steel. Weigh out accurately about 1 g. of the drillings or borings of the nickel steel‡ (or sufficient of the sample to contain 0·03 to 0·04 g. of nickel) into a 100 to 150 ml. beaker or porcelain basin, dissolve it in the minimum volume of concentrated hydrochloric acid (about 20 ml.

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* This is obtainable from the Mallinckrodt Chemical Works, U.S.A. ; see Section **A 9**. Alternatively, sufficient of a nickel salt to contain about 0·05 g. of nickel may be used.

† The sodium acetate method cannot be used in the presence of ferric iron ; ferrous iron does not interfere.

‡ Ridsdale's " Nickel Steel, No. 22 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Nickel Steel ' T^2 ' " (a British Chemical Standard) is suitable. Both steels contain about 4 per cent of nickel.

should suffice), and boil with successive additions of concentrated nitric acid (*ca.* 5 ml.) to ensure complete oxidation of the iron to the ferric state. Dilute somewhat, filter, if necessary, from any solid material, and wash the paper with hot water ; dilute the filtrate (or solution) to 250 ml. in a 400 ml. beaker. Add 5 g. of citric or tartaric acid, neutralise the solution with dilute ammonium hydroxide solution,* and then barely acidify (litmus) with dilute hydrochloric acid. Warm the solution to 60° to 80°C, add a slight excess of a 1 per cent alcoholic solution of dimethylglyoxime (25 to 30 ml.), immediately followed by dilute ammonia solution until the liquid is slightly ammoniacal, stir well, and allow to stand on the steam bath for 30 to 60 minutes. Filter off the precipitate through a weighed filter crucible ; test the filtrate for complete precipitation with a little dimethyl-glyoxime solution, and wash the precipitate with hot water until free from chloride.(1) Dry the precipitate at 110° to 120°C for 45 to 60 minutes, and weigh as $Ni(C_4H_7O_2N_2)_2$.

Calculate the percentage of nickel in the steel.

Note. 1. A rapid method for weighing the precipitate, collected in a sintered glass or porous porcelain crucible, is as follows (J. Dick, 1929). After washing the nickel dimethylglyoxime with cold water, wash 5 or 6 times with rectified spirit, followed by several times with small volumes of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible with a clean linen cloth, and leave in a vacuum desiccator for 10 minutes. Weigh as $Ni(C_4H_7O_2N_2)_2$.

For other methods for the determination of nickel, see Section **IV, 32.**

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* If a precipitate appears or if the solution is not clear when it is rendered ammoniacal, more tartaric or citric acid must be added until a perfectly clear solution is obtained upon adding dilute ammonia solution.

SYSTEMATIC GRAVIMETRIC ANALYSIS

IV, 13. General discussion.—In the succeeding Sections a brief account will be given of a number of selected methods for the gravimetric determinations of the various elements and radicals. It is believed that these will suffice to meet the needs of the student during the whole period of his training; for a more detailed study, particularly of the limitations of some of the various methods, reference must be made to other treatises.*

It has been considered expedient, following Hillebrand and Lundell, to treat the elements and radicals in the following order:

(*a*) Elements that give precipitates with hydrogen sulphide in acid solution: lead, silver, mercury, bismuth, cadmium, copper, arsenic, antimony, tin, molybdenum, selenium, tellurium, gold, palladium, platinum (thallium). Of these the sulphides of lead, silver, mercury, bismuth, cadmium, copper and palladium are insoluble in acids and in solutions of alkali sulphides.

(*b*) Elements that give precipitates with hydrogen sulphide in alkaline solution (or with ammonium sulphide): aluminium, beryllium, chromium, iron, nickel, cobalt, zinc, manganese, vanadium, uranium, thorium, cerium, titanium, zirconium, thallium. Of these, iron, nickel, cobalt, zinc, manganese, vanadium, uranium and thallium form sulphides that are soluble in acids, whilst the following elements form hydroxides or basic compounds: aluminium, chromium, beryllium, thorium, cerium, zirconium and titanium.

(*c*) The alkaline earth elements (calcium, strontium and barium) and magnesium.

(*d*) The alkali elements: sodium, potassium and lithium (ammonium).

(*e*) Tungsten.

(*f*) The anions in the empirical order: chloride, bromide, iodide, thiocyanate, cyanide, fluoride, chlorate, perchlorate, iodate, sulphate, sulphide, sulphite, thiosulphate, phosphate, phosphite, hypophosphite, oxalate, borate, silicate, fluosilicate, ferrocyanide, ferricyanide, nitrite, nitrate and carbonate.

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* For example: W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* (J. Wiley, 1929); G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis* (J. Wiley, 1938); J. W. Mellor and H. V. Thompson, *A Treatise on Quantitative Inorganic Analysis* (C. Griffin, 1938); G. E. F. Lundell, J. I. Hofmann, and H. A. Bright, *Chemical Analysis of Iron and Steel* (J. Wiley, 1931); W. W. Scott-N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. I (D. Van Nostrand Co.; The Technical Press, 1939).

IV, 14. LEAD

Discussion. Lead may be estimated in the following forms :

A. Lead sulphate, $PbSO_4$. This provides a separation from the numerous elements which form soluble sulphates. Calcium, strontium, barium, mercury, tungsten, silver, bismuth, antimony and silica all interfere to a greater or less extent. Hydrochloric and nitric acids exert a solvent action upon lead sulphate, hence if these are present, the solution must be evaporated twice with sulphuric acid until dense white fumes are evolved. Lead sulphate is slightly soluble in dilute sulphuric acid, although with the extremely dilute acid, the solubility is less than in water (0·0040 g. per litre at 18°C), owing to the common ion effect ; it is almost insoluble in alcohol. A satisfactory wash solution is a dilute solution of sulphuric acid that has been saturated with lead sulphate at the laboratory temperature.

At a red heat, it is easily reduced by carbonaceous matter, with loss of lead by volatilisation. For this reason the precipitate is best collected in a filtering crucible, and dried at 500° to 600°C.

B. Lead chromate, $PbCrO_4$. This determination is more accurate than **A**, but is limited in its applicability because of the general insolubility of chromates.

C. Lead molybdate, $PbMoO_4$. This is an excellent method since the substance has a high molecular weight, is less soluble than the sulphate, and suffers no change upon ignition. Substances which form insoluble molybdates (*e.g.*, the alkaline earth metals and cadmium), which are easily hydrolysed (*e.g.*, tin or titanium), and which form insoluble compounds with lead (*e.g.*, chromates, arsenates or phosphates) must be absent.

D. Lead dioxide, PbO_2. This excellent electrolytic method is described in Section **IV, 79.**

A. Determination of lead as sulphate. *Procedure.* Weigh out accurately about 0·3 g. of the lead salt* into a 10 cm. porcelain basin, dissolve it in about 20 ml. of water, add 2 ml. of pure concentrated sulphuric acid, evaporate the mixture as far as possible on the water bath, then on a sand bath, wire gauze or low temperature hot plate until thick white fumes of sulphuric acid are freely evolved. This ensures the complete removal of nitric acid and conversion of the lead salt into the sulphate.† Cool, dilute carefully with 40 ml. of water (the final solution should contain about 4 ml. of concentrated sulphuric acid in 100 ml. of solution), mix thoroughly, and allow to stand for at least an hour. Filter off the precipitate of lead sulphate through a weighed porcelain or silica Gooch crucible or through a porous porcelain filtering crucible. Wash the precipitate three times with 3 per cent (by volume) sulphuric acid saturated with lead sulphate (compare Section **IV, 57A**). Dry the crucible and contents at 100°C for 1 hour, and then place it inside a nickel crucible (Fig. 2-33) and heat gradually to a dull red heat (500° to 600°C) until constant weight is obtained. Alternatively, the precipitate, collected on a sintered glass or porous porcelain crucible and washed as above, may be washed with rectified spirit until free from sulphate (1), and then dried at 130°C to constant weight. Weigh as $PbSO_4$.

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* A.R. lead nitrate is suitable. If the substance is insoluble in water, dissolve it in the minimum quantity of nitric acid.

† For work demanding the highest accuracy, allow to cool, wash down the sides of the dish, and repeat the evaporation.

Calculate the percentage of lead in the sample. Weigh as $PbSO_4$.*

Note. 1. For the rapid weighing of the lead sulphate, the alcohol washing is followed by several washings with small volumes of anhydrous ether, and the precipitate is sucked dry at the pump for 10 minutes. The outside of the crucible is then wiped with a clean linen cloth, left in a vacuum desiccator for 10 minutes, and weighed (J. Dick, 1929).

B. Determination of lead as chromate. *Procedure* (compare Section **III, 109**). Weigh out 0·3 g. of the lead salt (1), dissolve it in 150 ml. of water, and add dilute acetic acid to the solution until it is distinctly acid. Heat to boiling, add from a pipette 4 per cent potassium chromate solution in slight excess (10 ml. will usually suffice). Boil gently for 5 to 10 minutes (or until the precipitate settles) ; the supernatant liquid must be coloured slightly yellow. Filter through a Gooch, sintered glass or porous porcelain filtering crucible, wash thoroughly with a hot dilute solution of sodium acetate or with hot water. Dry at 120°C to constant weight. Weigh as $PbCrO_4$.

Note. 1. A.R. lead nitrate is suitable for practice in this estimation. If the solution is neutral or basic, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate (5 to 10 g.) to replace the nitric acid by acetic acid.

C. Determination of lead as molybdate. *Procedure.* Weigh out 0·3 g. of the lead salt, dissolve it in 200 ml. of water, and add 4 drops of concentrated nitric acid. Heat to boiling, and slowly add from a burette or pipette, with stirring, a 2·5 per cent aqueous solution of ammonium molybdate. When precipitation appears to be complete, boil for 1 minute, allow the precipitate to settle, and add a few drops of the precipitant to the supernatant liquid. If a precipitate forms, repeat the process until the ammonium molybdate is present in *slight* excess. When precipitation is complete, add dilute ammonia solution (1 : 2) dropwise until the solution is neutral or slightly alkaline to litmus. Acidify with a few drops of acetic acid, and allow to stand for a few minutes. Decant the supernatant liquid through a weighed porcelain or silica Gooch crucible (or through a porcelain filter crucible), and wash the precipitate 3 or 4 times by decantation with 75 ml. portions of 2 per cent ammonium nitrate solution. Transfer the precipitate to the filter, and wash until the washings give no test for molybdenum (*e.g.*, no brown precipitate with potassium ferrocyanide solution). Place the filter crucible inside a nickel crucible or in a radiator (Fig. 2-14), and gradually heat to dull redness. Maintain the crucible at dull redness for 10 minutes, cool in a desiccator and weigh. Repeat the heating, etc., until constant weight is attained. Weigh as $PbMoO_4$.

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* The conversion factors for all the determinations described in this and the following Sections are collected in the Appendix (Section **A, 2**).

IV, 15. SILVER

Discussion. This element is usually determined as **silver chloride, AgCl.** The theory of the process has been given under Chloride (Section **IV, 5**). Lead, cuprous, palladous, mercurous and thallous ions interfere as do cyanides and thiosulphates. If a mercurous (or cuprous or thallous) salt is present, it must be oxidised with concentrated nitric acid before the precipitation of silver ; this process also destroys cyanides and thiosulphates. If lead is present, the solution must be diluted so that it contains not more than 0·25 g. of the substance in 200 ml., and the hydrochloric acid must be added very slowly.

Silver may also be determined electrolytically ; for details see Section **IV, 83.**

Determination of silver as chloride. *Procedure.* The solution (200 ml.) should contain about 0·1 g. of silver (1) and about 1 per cent by volume of nitric acid. Heat to about 70°C, and add approximately 0·2*N* pure hydrochloric acid slowly and with constant stirring until no further precipitation occurs ; avoid a large excess of the acid. Warm until the precipitate settles, allow to cool to about 25°C, and test the supernatant liquid with a few drops of the acid to be sure that precipitation is complete. Allow the precipitate to settle in a dark place for several hours or, preferably, overnight.

Pour the supernatant liquid through a weighed Gooch or sintered glass or porous porcelain crucible, wash the precipitate by decantation with 0·1*N* nitric acid, transfer the precipitate to the crucible, and wash again with 0·01*N* nitric acid until free from chloride. Dry the precipitate first at 100°C and then at 130° to 150°C, allow to cool in a desiccator and weigh. Repeat the heating, etc., until constant weight is obtained (2). Weigh as AgCl.

Notes. 1. For example, from 0·2 g. of A.R. silver nitrate.
2. See footnote in Section **IV, 5.**

IV, 16. MERCURY

Discussion. Mercury may be estimated in the following forms:

A. Mercuric sulphide, HgS. The precipitation of mercury in hydrochloric acid solution by hydrogen sulphide as mercuric sulphide is an accurate procedure in the absence of copper, cadmium, tin, zinc and thallium; the latter metals complicate reactions which are based upon the behaviour of pure mercuric sulphide. Unless the experimental conditions detailed below are strictly followed, the precipitate is liable to be contaminated with a little sulphur, which must be removed by extraction with carbon disulphide. Oxidising agents (nitric acid, chlorine, ferric chloride, etc.) must be absent.

B. Mercury zinc thiocyanate, $Hg[Zn(CNS)_4]$. This method is based upon the precipitation of mercury from mercuric compounds in neutral or acid solutions as mercuric zinc thiocyanate with a reagent which contains 39 g. of ammonium thiocyanate and 29 g. of zinc sulphate per litre. For quantitative precipitation not more than 5 per cent of free acid should be present in the solution before the addition of the precipitating agent. If a larger quantity of acid is present, it must be neutralised with sodium hydroxide solution: ammonia solution should not be used because an excessive quantity of ammonium salts exerts a solvent action upon the precipitate. Cadmium, cobalt, copper, bismuth, manganese and mercurous compounds must be absent since they give insoluble thiocyanates with the reagent; small quantities of nickel do not interfere.

C. Copper ethylenediamine mercuri-iodide $[Cu\ en_2][HgI_4]$; ethylenediamine method. This is a rapid method for the determination of mercury.

For further discussion, see Section **I, 62P.**

A. Determination of mercury as sulphide. *Procedure.* Weigh out accurately about 0·15 g. of the mercuric salt (1), dissolve it in 100 ml. of water, and add a few ml. of dilute hydrochloric acid. Saturate the cold solution with washed hydrogen sulphide (2), allow the precipitate to settle, and filter through a weighed Gooch, sintered glass or porous porcelain crucible. Wash the precipitate with cold water (3), and weigh it, as HgS, after drying at 105° to 110°C (4).

Notes. 1. A.R. mercuric chloride is suitable. Alternatively, the solution should contain not more than 0·1 g. of mercuric mercury per 100 ml., and should be free from oxidising agents.

2. The colour of the mercuric sulphide precipitate will become perfectly black as soon as the liquid is saturated with the gas.

3. If the presence of sulphur is suspected, the precipitate is washed with hot water, alcohol, carbon bisulphide, or alcohol + ether, and then dried at 105° to 110°C.

4. A rapid method for weighing the precipitate, collected in a sintered glass or porous porcelain crucible, is as follows (J. Dick, 1929). After washing the mercuric sulphide with cold water, wash it 5 or 6 times with rectified spirit, followed by several times with small volumes of anhydrous ether, and then suck the precipitate dry on the pump for 10 minutes. Wipe the outside of the crucible dry with a clean linen cloth and leave in a vacuum desiccator for 10 minutes. Weigh as HgS.

B. Determination of mercury as mercuric zinc thiocyanate. *Procedure.* Weigh out accurately about 0·2 g. of the mercuric salt (*e.g.*, A.R. mercuric chloride) into a 250 ml. beaker, and dissolve it in 100 ml. of cold water containing 2 drops of concentrated hydrochloric acid. Add 25 ml. of the ammonium thiocyanate-zinc sulphate reagent (see *Discussion*). Stir vigorously with a previously moistened glass rod for 2 to 3 minutes, but avoid touching the walls of the beaker. The initially clear liquid gradually becomes turbid during the stirring, and a white crystalline precipitate slowly forms. Allow the contents of the beaker to stand for at least 2 hours. Filter the precipitate on a weighed sintered glass or porous porcelain crucible; transfer the precipitate to the crucible with the aid of a wash-liquid composed of 5 ml. of the precipitating reagent and 450 ml. of water. (The precipitate is slightly soluble in water, but practically insoluble in the special wash liquid.) Finally, wash the precipitate 5 times with the special wash-liquid, and then once with a little water to remove the adhering wash-liquid. Dry the crucible and precipitate in an electric oven maintained at 105° ± 2°C until constant in weight. Weigh as $Hg[Zn(CNS)_4]$.

C. Determination of mercury by the ethylenediamine method. *Procedure.* The neutral or faintly ammoniacal mercury solution should occupy a volume of 80 to 500 ml., and contain not more than about 0·2 g. Hg. Treat with excess (say, 2-3 g.) of KI in the form of a 2% solution, heat nearly to boiling and precipitate with a boiling, concentrated aqueous solution of copper ethylenediamine nitrate $[Cu\ en_2](NO_3)_2$ or of the corresponding sulphate (Section **I, 62P**). Allow to cool to room temperature and filter off the dark blue-violet, crystalline complex $[Cu\ en_2][HgI_4]$ on a weighed crucible (Gooch, sintered glass or porous porcelain). Wash 3 to 6 times with a solution containing 0·2 g. of KI and 0·2 g. of $[Cu\ en_2](NO_3)_2,2H_2O$ (or the corresponding sulphate) in 200 ml. of water. To remove the water adhering to the wall of the crucible, wash 3 or 4 times with 2 ml. portions of 95 per cent alcohol and finally 3 or 4 times with 2 ml. portions of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, and dry the precipitate for 10 minutes (or to constant weight) in a vacuum desiccator. Weigh as $[Cu\ en_2][HgI_4]$.

For **the determination of mercury in aqua regia solution** (up to 0·3 g. Hg in 100 to 200 ml.), render the solution faintly alkaline with ammonia solution, add a large excess of potassium iodide (say, 3 to 4 g. KI in the form of a 2 per cent solution), heat to boiling and precipitate as above. When precipitation is complete, dilute with one-quarter of the total volume with distilled water, allow to cool slowly to room temperature, and complete the determination as already detailed.

IV, 17. BISMUTH

Discussion. Bismuth may be satisfactorily determined in the following forms :

A. Bismuth oxyiodide, BiOI. The cold bismuth solution, weakly acid with nitric acid, is treated with an excess of potassium iodide when BI_3 and some $K[BiI_4]$ are formed :

$$Bi(NO_3)_3 + 3KI = BiI_3 + 3KNO_3\,;$$
$$BI_3 + KI = K[BiI_4].$$

Upon dilution and boiling, bismuth oxyiodide is formed, and is weighed as such after suitable drying.

$$\underset{\text{(black)}}{BI_3} + H_2O = BiOI + 2HI\,;$$
$$\underset{\text{(yellow)}}{K[BiI_4]} + H_2O = BiOI + KI + 2HI.$$

A large excess of potassium iodide should be avoided since the complex salt is not so readily hydrolysed as the tri-iodide. This is an excellent method, because the oxyiodide is precipitated in a form which is very convenient for filtration and weighing.

B. Bismuth pyrogallate, $Bi(C_6H_3O_3)$. The precipitation of bismuth with pyrogallol is quantitative only if the acidity (hydrochloric, sulphuric or nitric acid) does not exceed 0·1*N*. The method is an excellent one for the determination of bismuth in the presence of lead.

C. Bismuth oxide, Bi_2O_3, through the cupferron complex. The bismuth in hydrochloric or nitric acid solution is precipitated as the cupferron complex (see Section **I, 62B**), and the latter is converted by ignition into, and weighed as, Bi_2O_3. This procedure separates bismuth from cadmium, lead, arsenic, mercury, antimonic and zinc ions.

D. Bismuth "oxinate," $Bi(C_9H_6ON)_3$. This method uses oxine as the precipitating agent. For the advantages and limitations of this versatile reagent, see Section **I, 62C.** Halogens must be absent as there is a tendency for compounds of the general formula $(C_9H_7ON)HBiX_4$ (where X = halogen) to be precipitated.

A. Determination of bismuth as oxyiodide. *Procedure.* The cold bismuth nitrate solution, containing 0·1 to 0·15 g. of Bi (1), must be slightly acid with nitric acid (2), and occupy a volume of about 20 ml. Add finely-powdered solid potassium iodide, slowly and with stirring, until the supernatant liquid above the black precipitate of bismuth tri-iodide is just coloured yellow (due to $K[BiI_4]$). Dilute to 200 ml. with boiling water, and boil for a few minutes. The black tri-iodide is converted into the copper-coloured precipitate of the oxyiodide. The supernatant liquid should be colourless; if this is yellow, a further 100 ml. of water should be added, and the boiling continued until colourless. Add a few drops of methyl orange indicator, and then sodium acetate solution (25 g. per litre) from a burette until the solution is neutral. Filter off the precipitate through a weighed Gooch, sintered glass or porous porcelain crucible, wash with hot water, and dry at 105° to 110°C to constant weight. Weigh as BiOI.

Notes. 1. A suitable solution for practice can be obtained by dissolving about 0·15 g. of pure bismuth (the A.R. product is obtainable from the Mallinckrodt Chemical Works, U.S.A.; see Section **A, 9**), accurately weighed, in the minimum volume of 1 : 4 nitric acid.

2. Chloride and bromide should be absent. If the solution is strongly acid with nitric acid, it should be evaporated to dryness on the water bath, and dissolved in a little dilute nitric acid.

B. Determination of bismuth as pyrogallate. *Procedure.* The solution (150 ml.) should be weakly acid with nitric acid and contain 0·1 to 0·2 g. of Bi. Treat the solution with dilute ammonia solution until a permanent turbidity is obtained; render the solution clear by the cautious addition of a little dilute nitric acid. Heat to boiling, and add a slight excess of a solution of pure pyrogallol (Section **I, 62, O**) in air-free water. A yellow, finely crystalline precipitate is immediately formed. Boil for a short time, test for completeness of precipitation with a little of there agent, dilute slightly, and filter through a weighed sintered glass or porous porcelain crucible after the precipitate settles out. Wash with 0·05*N* nitric acid, and finally with water. Dry to constant weight at 110°C. Weigh as $Bi(C_6H_3O_3)$.

C. Determination of bismuth as oxide after precipitation as the cupferron complex. *Procedure.* Treat the aqueous bismuth nitrate solution (200 ml.) with freshly prepared 6 per cent aqueous cupferron solution until there is present at least three times of cupferron as of bismuth (*i.e.*, $\nless$ 0·3 g. per 0·1 g. Bi). Heat the solution to boiling, add ammonia solution until the liquid is alkaline (litmus paper), followed by dilute nitric acid until it is just acid. Filter the precipitate through a quantitative filter paper, and wash with 0·1 per cent cupferron solution containing a few drops of dilute nitric acid. Ignite in a crucible in the usual manner (Section **II, 36**), and finally with free access of air over the full flame of a Bunsen burner to constant weight. Weigh as Bi_2O_3.

D. Determination of bismuth with "oxine." *Procedure.* The solution of bismuth nitrate (100 ml.) should contain sufficient tartaric acid to prevent precipitation in the following stages. Add a drop or two of phenolphthalein, and then dilute ammonia solution until the indicator is just pink. Acidify with acetic acid, and add 1 to 2 g. of ammonium or sodium acetate for each 0·05 g. of Bi expected to be present. Heat to 60° to 70°C, treat rapidly with a saturated alcoholic solution of oxine (excess is without influence), then heat almost to boiling, and allow to cool. Filter off on a weighed sintered glass or porous porcelain crucible, wash with hot water, and dry to constant weight at 130° to 140°C. Weigh as $Bi(C_9H_6ON)_3$.

IV, 18. CADMIUM

Discussion. Cadmium may be determined in the following forms :

A. Cadmium molybdate, $CdMoO_4$. The method is of limited application, since all metals other than magnesium and the alkali metals must be absent.

B. Cadmium β-naphthaquinoline complex, $[(C_{13}H_9N)_2H_2]CdI_4$. This method permits of the separation of cadmium from relatively large quantities of zinc, iron, chromium, aluminium, cobalt, nickel, manganese and magnesium, and also from antimony and tin if ammonium oxalate or larger amounts of sodium tartrate are used.

C. Cadmium quinaldinate, $Cd(C_{10}H_6O_2N)_2$. Quinaldinic acid or its sodium salt precipitates cadmium quantitatively from acetic acid or neutral solutions. The precipitate is collected on a Gooch type of crucible, and dried at 125°C. A determination may be completed in about 90 minutes. For the limitations of the method, see Section **I, 62N.**

D. $[Cd(C_5H_5N)_2](CNS)_2$; pyridine method. If a hot neutral or faintly acid solution of a cadmium salt is treated with ammonium thiocyanate and pyridine, dipyridine cadmium thiocyanate is quantitatively precipitated. This precipitate is collected, and washed *inter alia* with alcohol and ether containing a little pyridine; it may be dried simply by leaving in a vacuum desiccator for 15 to 20 minutes. A determination can thus be completed in less than an hour. The limitations of the method are discussed under Copper (Section **IV, 19E**). If the solution is weakly acid, ammonium thiocyanate may be added, followed by pyridine, until a precipitate just forms, the latter dissolved by warming, and a further 1 ml. of pyridine added.

E. Metallic cadmium. This excellent electrolytic method is described in Section **IV, 80.**

A. Determination of cadmium as molybdate. *Procedure.* Weigh out accurately 0·4 to 0·5 g. of the cadmium salt (1), dissolve it in 100 ml. of water, render the solution just alkaline with ammonia solution, and then feebly acid with acetic acid. Treat the boiling solution dropwise and with constant stirring (2) with a solution of ammonium molybdate (3) in slight excess (4), and maintain the mixture at about 90°C until the precipitate has settled. Allow to stand for at least 2 hours, but preferably overnight. Filter off the precipitate of cadmium molybdate upon a weighed sintered glass crucible of fine porosity, or upon a Gooch crucible covered with a layer of ground asbestos, wash with hot water, and dry at 120°C to constant weight. Weigh as $CdMoO_4$.

Notes. 1. A.R. cadmium iodide is a suitable salt to employ for practice in this determination.

2. The precipitate adheres very tenaciously to the glass if this is touched with the stirring rod during precipitation. Touching of the sides of the glass vessel with the stirring rod should therefore be avoided.

3. This solution is prepared by stirring up 15 g. of A.R. molybdenum trioxide with 200 ml. of water, adding a few drops of phenolphthalein, and then concentrated ammonia solution with constant stirring until the oxide is dissolved. Acetic acid is then added until the pink colour disappears, but the reaction is acid to litmus. Filter and dilute to 500 ml. 1 Ml. of this reagent will precipitate 0·02 g. of Cd.

4. Add a drop of the supernatant solution to a saturated solution of pyrogallol in chloroform; a brown colouration is produced if excess of molybdate is present.

B. Determination of cadmium as the β-naphthaquinoline complex. *Procedure.* The cadmium salt solution, containing about 0·15 g. of Cd, should occupy a volume of about 50 ml.

and be $2N$ with regard to sulphuric acid. Add 50 ml. of 10 per cent sodium tartrate solution, followed successively by a 2·5 per cent solution of β-naphthaquinoline in $0{\cdot}5N$ sulphuric acid, a few drops of dilute sulphuric acid, and then $0{\cdot}2N$ potassium iodide in excess. After 20 minutes, filter the precipitate of the cadmium complex through a weighed Gooch, sintered glass or porous porcelain crucible, wash with a solution containing 10 ml. of $0{\cdot}2N$ potassium iodide, 10 ml. of 2·5 per cent β-naphthaquinoline in $0{\cdot}5N$ sulphuric acid, 80 ml. of water and 1 to 2 drops of dilute sulphurous acid, and finally suck as free as possible from the wash liquor. Dry the precipitate to constant weight at 130°C. Weigh as $[(C_{13}H_9N)_2H_2](CdI_4)$.

C. Determination of cadmium as quinaldinate. *Procedure.* The solution (150 ml.) should be neutral or weakly acid with acetic acid, and should contain 0·1 to 0·15 g. of Cd. Heat the solution to boiling, and remove the source of heat. Add the reagent (a 3·3 per cent solution of quinaldinic acid or of the sodium salt in water) dropwise with vigorous stirring until present in slight excess. Then neutralise carefully with dilute ammonia solution, and allow the white curdy precipitate to settle. When cold, wash with cold water by decantation, filter through a sintered glass or porous porcelain crucible, wash thoroughly with cold water, and dry at 125°C to constant weight. Weigh as $Cd(C_{10}H_6O_2N)_2$.

D. Determination of cadmium by the pyridine method. *Procedure.* The solution (75 to 100 ml.) should contain about 0·1 g. of Cd (1) and be neutral or very feebly acid. Add 0·5 to 1·0 g. of A.R. ammonium thiocyanate, stir, heat to boiling, and treat the solution with 1 ml. of pure pyridine dropwise and with stirring. The complex slowly separates as the solution cools. Filter the *cold* solution through a weighed sintered glass or porous porcelain crucible, transfer the precipitate to the crucible with the aid of *solution 1.* Wash 4 to 5 times with *solution 2,* then twice with 1 ml. portions of *solution 3,* and finally 5 to 6 times with small volumes (*ca.* 1 ml.) of *solution 4.* (For further experimental details, see under Copper, Section **IV, 19E,** and Zinc, Section **IV, 34D.**) Dry the precipitate in a vacuum desiccator (Fig. 2-10) for 10 to 15 minutes and weigh. Repeat the drying until constant weight is attained. Weigh as $[Cd(C_5H_5N)_2](CNS)_2$.

Solution 1. 100 Ml. of water containing 0·3 g. of NH_4CNS and 0·5 ml. of pyridine.

Solution 2. 73 Ml. of water, 25 ml. of 95 per cent alcohol, 0·1 g. of NH_4CNS, and 2 ml. of pyridine.

Solution 3. 10 Ml. of absolute alcohol and 1 ml. of pyridine.

Solution 4. 15 Ml. of absolute (sodium dried) ether and 2 drops of pyridine.

Note. 1. For practice in this determination the student may employ about 0 3 g., accurately weighed, of A.R. cadmium sulphate or of A.R. cadmium iodide.

IV, 19. COPPER

Discussion. Copper may be determined in the following forms :

A. Cuprous thiocyanate, $Cu_2(CNS)_2$. This is an excellent method since most thiocyanates of the metals are soluble. Separation may thus be effected from bismuth, cadmium, arsenic, antimony, tin, iron, nickel, cobalt, manganese and zinc. The addition of 2 to 3 g. of tartaric acid is desirable for the prevention of hydrolysis when bismuth, antimony or tin are present. Excessive amounts of ammonium salts or of the thiocyanate precipitant should be absent as should also oxidising agents and high acidity. Lead, mercury, the precious metals, selenium and tellurium interfere and contaminate the precipitate.

B. Copper benzoinoxime, $Cu(C_{14}H_{11}O_2N)$. α-Benzoinoxime (cupron) is a specific reagent for the determination of copper in ammoniacal solutions (compare Section **I, 62D**). A green, heavy and readily filterable precipitate is obtained : this is insoluble in water, dilute ammonia solution, acetic acid, tartaric acid and alcohol, is slightly soluble in concentrated ammonia solution, and readily soluble in mineral acids. Precipitation is quantitative in ammoniacal tartrate solutions : separation can thus be effected from iron and other metals whose hydroxides are not precipitated in tartrate solutions. Separation can also be made from cadmium, zinc, cobalt and nickel, which are not precipitated in ammoniacal solutions.

C. Copper salicylaldoxime, $Cu(C_7H_5O_2N)_2$. In this method silver, mercuric, arsenious, ferric, nickel, cobalt and zinc ions do not interfere provided the solution contains sufficient acetic acid ; the copper complex alone is insoluble in acetic acid. In neutral or in very faintly acid solution nickel and cobalt are precipitated, but the other ions remain in solution. An excellent method for the separation of copper and nickel is thus available (see Section **IV, 32B**).

D. Copper quinaldinate, $Cu(C_{10}H_6ON_2)_2,H_2O$. Quinaldinic acid or its sodium salt is a specific reagent for copper if precipitation is made in sulphuric acid solution and iron and zinc are absent (compare Section **I, 62N**). With this reagent, a determination of copper may be completed in 2 hours.

E. $[Cu(C_5H_5N)_2](CNS)_2$; pyridine method. If a neutral or faintly acid copper solution is treated with ammonium thiocyanate and pyridine, dipyridine copper dithiocyanate is quantitatively precipitated. This precipitate is collected and washed *inter alia* with alcohol and ether containing a little pyridine, and then dried simply by leaving in a vacuum desiccator for 10 to 20 minutes. A determination can be completed in less than 1 hour. This rapid method is applicable in the absence of cadmium, nickel, cobalt, zinc and manganese (see Section **I, 62L**). Large quantities of ammonium salts must be absent as these exert a solvent action upon the precipitate. If the solution is strongly acid, it must be evaporated to dryness and the residue dissolved in water.

F. Copper ethylenediamine mercuri-iodide $[\text{Cu en}_2][\text{HgI}_4]$; **ethylenediamine method.** This, like **E,** is a rapid method for the determination of copper. Owing to the small conversion factor (0·07126) the procedure is valuable for the determination of small amounts of copper.

For further discussion, see Section **I, 62P.**

G. Metallic copper. The electrolytic method is one of the best for the determination of copper. Comparatively large quantities (up to 5 g.) can be handled (see Section **IV, 78** for details).

A. Determination of copper as cuprous thiocyanate. *Procedure.* Weigh out accurately about 0·4 g. of the copper salt (1) into a 250 ml. beaker, and dissolve it in 50 ml. of water. Add a few drops of dilute hydrochloric acid, and then a slight excess (2 to 3 ml.) of freshly-prepared saturated sulphurous acid solution. Dilute the cold liquid to about 150 ml., heat to boiling, and add freshly-prepared 10 per cent ammonium thiocyanate solution, slowly and with constant stirring, from a burette until present in *slight* excess. The precipitate of cuprous thiocyanate should be white ; the mother liquor should be colourless and smell of sulphur dioxide. Allow to stand for several hours, but preferably overnight. Filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), and wash the precipitate 10 to 15 times with a cold solution prepared by adding to every 100 ml. of water 1 ml. of a 10 per cent solution of ammonium thiocyanate and 5 to 6 drops of saturated sulphurous acid solution, and finally several times with 20 per cent alcohol to remove ammonium thiocyanate (2). Dry the precipitate to constant weight at 110° to 120°C (3). Weigh as $\text{Cu}_2(\text{CNS})_2$.

Notes. 1. A.R. copper sulphate pentahydrate is suitable for practice in this determination. 0·4 Gram of this contains about 0·1 g. of Cu.

2. Alternatively, but less desirably, the precipitate may be washed with cold water until the filtrate gives only a slight reddish colouration with ferric chloride, and finally with 20 per cent alcohol.

3. The precipitate, collected in a sintered glass or porous porcelain crucible, may be weighed more rapidly as follows (J. Dick, 1930). Wash the cuprous thiocyanate 5 or 6 times with rectified spirit, followed by a similar treatment

with small volumes of anhydrous ether, then suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible with a clean linen cloth and leave in a vacuum desiccator for 10 minutes. Weigh as $Cu_2(CNS)_2$.

B. Determination of copper with α-benzoinoxime. *Procedure.* Treat the neutral solution, which should be free from ammonium salts and contain not more than 0·05 g. of copper, with dilute ammonia solution until a clear blue solution is obtained. Heat to boiling and precipitate the copper by the addition, dropwise, of a 2 per cent alcoholic solution of the reagent. Precipitation is complete when the blue colour of the solution disappears. Filter the heavy green precipitate on a weighed sintered glass or porous porcelain crucible, wash with hot 1 per cent ammonia solution, then with warm alcohol, and finally with hot water. Dry to constant weight at 105° to 115°C. Weigh as $Cu(C_{14}H_{11}O_2N)$. It is recommended that completeness of washing be tested for by washing the dry precipitate with warm alcohol followed by hot water. Dry again to constant weight at 105° to 115°C.

C. Determination of copper with salicylaldoxime. *Procedure.* Add 2*N* sodium hydroxide to the copper solution (100 ml.), containing 0·05 to 0·1 g. of Cu, until a slight permanent precipitate is formed, and dissolve this by the addition of a little dilute acetic acid.* Add the salicylaldoxime reagent (for preparation, see Section **I, 62E**) in *slight* excess at room temperature. Filter off the precipitated complex on a weighed sintered glass or porous porcelain crucible, wash with water until the washings give no colour with ferric chloride, and dry to constant weight at 100° to 105°C (about 1 hour). Weigh as $Cu(C_7H_5O_2N)_2$. Decomposition occurs above 115°C.

D. Determination of copper as quinaldinate. *Procedure.* Acidify the solution (*ca.* 150 ml.), containing up to 0·1 g. of copper, with 2 to 5 ml. of 2*N* sulphuric acid, heat to boiling, and add the reagent (for preparation, see Section **I, 62N**) slowly and with stirring until present in slight excess. The green crystalline precipitate of copper quinaldinate separates out immediately. Wash with hot water by decantation, then transfer to a weighed sintered glass or porous porcelain crucible and wash with hot water until the excess of the reagent is removed. Dry at 125°C to constant weight. Weigh as $Cu(C_{10}H_6O_2N)_2,H_2O$.

E. Determination of copper by the pyridine method. *Procedure.* The solution (100 ml.) should contain not more than

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* Quantitative precipitation of copper commences at *p*H 2·6.

0·1 g. of Cu (1) and be neutral or very faintly acid. Add pure pyridine dropwise until the colour of the solution is practically azure-blue (1 to 2 ml. should suffice), then add 0·5 g. of solid A.R. ammonium thiocyanate, and stir vigorously. After a few minutes, collect the precipitate on a weighed sintered glass or porous porcelain crucible; transfer the precipitate to the crucible with the aid of *solution 1*. Wash the precipitate 6 to 8 times with *solution 2*, then wash the walls of the crucible 2 to 3 times with 1·5 ml. portions of *solution 3* (use a 2 ml. pipette for this purpose), and finally several times with small volumes (1 to 2 ml.) of *solution 4*. It is important to suck the precipitate almost dry between each washing; it is advisable also to stir the precipitate with a thin glass rod during the washing with *solutions 3* and *4*. Dry the crucible and precipitate in a vacuum desiccator (Fig. 2-10) for 5 to 20 minutes, according to its weight. Repeat the drying until constant weight is attained. Weigh as $[Cu(C_5H_5N)_2](CNS)_2$.

Solution 1. 100 Ml. of water containing 0·3 g. of NH_4CNS and 0·3 ml. of pyridine.

Solution 2. 80 Ml. of 95 per cent alcohol, 19·2 ml. of water, 0·8 ml. of pyridine, and 0·05 g. of NH_4CNS.

Solution 3. 10 Ml. of absolute alcohol + 2 drops of pyridine.

Solution 4. 20 Ml. of absolute (sodium dried) ether + 2 drops of pyridine.

Note. 1. For practice in this determination, the student may employ *ca.* 0·25 g., accurately weighed, of A.R. copper sulphate.

F. Determination of copper by the ethylenediamine method. *Procedure.* The solution should be neutral or very faintly acid and should contain up to 0·10 g. of Cu in a volume of 100 to 1000 ml. The experimental details for a volume of 100 ml. will be given. Treat the solution dropwise with an aqueous solution of ethylenediamine until the characteristic colouration of the $[Cu\ en_2]^{++}$ ion appears; add a little more of the reagent, followed by 1 to 2 g. of solid ammonium nitrate and 2 g. of potassium iodide. Heat to boiling, add a hot concentrated solution of potassium mercuri-iodide (1) to precipitate the complex. Allow to cool slowly with frequent stirring of the solution. When cold, filter off the precipitated complex $[Cu\ en_2][HgI_4]$ through a weighed crucible (Gooch, sintered glass or porous porcelain); transfer the precipitate to the crucible with the aid of a wash-liquid containing 0·1 g. of mercuric chloride, 2 g. of potassium iodide, 1 g. of ammonium nitrate and 2 to 3 drops of ethylenediamine per 100 ml., and wash it several times with the solution. Wash the walls of the crucible 4 times with 2 ml. portions of 95 per cent alcohol (rectified spirit), followed by 3 to 4 times with 2 ml. portions of anhydrous ether, and then suck the precipitate dry at the pump for 10 minutes. Dry the outside of the crucible with a clean linen cloth, leave it in a vacuum desiccator for 10 minutes, and weigh. Repeat the final drying in the desiccator until the weight is constant. Weigh as $[\mathrm{Cu\ en_2}][\mathrm{HgI_4}]$.

Note. 1. The potassium mercuri-iodide solution is prepared by treating aqueous mercuric chloride with a slight excess of potassium iodide solution.

IV, 20. ARSENIC

Discussion. Arsenic may be determined in the following forms :

A. Arsenic trisulphide, As_2S_3. The arsenic must be present in the tervalent state. Arsenic in the tervalent state (ensured by the addition of, for example, ferrous sulphate, cuprous chloride, pyrogallol or phosphorous acid) may be separated from other elements by distillation from a hydrochloric acid solution, the temperature of the vapour being held below 108°C ; arsenic trichloride alone (also germanium chloride, if present) volatilises and is collected in water or in hydrochloric acid.

B. Magnesium pyroarsenate, $Mg_2As_2O_7$. Here the arsenic must be present in the quinquevalent state (*e.g.*, as arsenate). Phosphates and other substances which give a precipitate with magnesia mixture must be absent, as must also organic matter, for this reduces the substance and arsenic is volatilised.

C. Ammonium uranyl arsenate, $NH_4UO_2AsO_4, xH_2O$, and subsequent weighing as uranous uranate, U_3O_8. The addition of a uranyl salt solution to an *arsenate* solution containing excess of ammonium ions results in the precipitation of ammonium uranyl arsenate, which is soluble in mineral acids but insoluble in acetic acid. Upon igniting the precipitate, the arsenic is completely volatilised, leaving a moss-green residue which consists mainly of U_3O_8 : this residue is dissolved in concentrated nitric acid, and the resultant uranyl nitrate upon cautious evaporation and subsequent ignition yields pure black U_3O_8, and is weighed in this form (D. T. Lewis and V. E. Davis, 1939).

If the solution contains arsenite, the latter must first be oxidised to arsenate with $0{\cdot}1N$ potassium bromate in hydrochloric acid solution at 70°C in the usual way (Section **III, 137**). A method is thus available for the **determination of arsenite and arsenate in admixture.** The arsenite is first determined with standard potassium bromate solution, and the total arsenate in the resulting liquid is then determined by precipitation as the uranium salt.

A. Determination of arsenic as trisulphide. *Procedure.* Pass a rapid stream of washed hydrogen sulphide through a solution of the arsenious arsenic (1) in 9*N* hydrochloric acid at 15° to 20°C. Allow to stand for an hour or two, and filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain) (2). Wash the precipitate with 8*N* hydrochloric acid saturated with hydrogen sulphide, then successively with alcohol, carbon disulphide (to remove any free sulphur which may be present) and alcohol. Dry at 105°C to constant weight, and weigh as As_2S_3.

Notes. 1. A suitable solution for practice in this estimation is prepared by dissolving about 0·3 g. of A.R. arsenious oxide, accurately weighed, in 9*N* hydrochloric acid.

2. Sometimes a film of arsenious sulphide adheres to the glass vessel in which precipitation was carried out; this can be dissolved in a little ammonia solution and the sulphide reprecipitated with the acid washing liquor.

B. Determination of arsenic as magnesium pyroarsenate. *Procedure.* The solution must contain all the arsenic as arsenate, and have a volume of not more than 100 ml. per 0·1 g. of arsenic. Add 5 ml. of concentrated hydrochloric acid slowly and with constant stirring to the arsenate solution (100 ml.) (1). Add a few drops of methyl red indicator, followed by 10 to 15 ml. of magnesia mixture (2) for each 0·1 g. of As present; the magnesia mixture must be added dropwise and with continuous stirring. Cool the solution in ice water, and add pure concentrated ammonia solution slowly and with constant stirring until the solution is alkaline. Stir the liquid for a few minutes, and add 10 ml. of concentrated ammonia solution. Allow the solution to stand at room temperature for at least 4 hours, but preferably overnight. Filter the precipitate through a weighed filter crucible (silica Gooch or porous porcelain), wash with cold 1 : 25 ammonia solution until free from chloride, and then remove as much as possible of the liquid by suction. Dry the precipitate at 100°C for 1 to 2 hours, place the crucible inside a nickel crucible (Fig. 2-33), and apply heat slowly at first until no more ammonia is evolved, and finally at the full temperature of a Méker type burner for 10 minutes (3). Cool in a desiccator and weigh. Repeat the heating, etc., until constant weight is attained. Weigh as $Mg_2As_2O_7$ (4).

Notes. 1. A suitable solution for practice is prepared by dissolving about 0·5 g., accurately weighed, of pure sodium arsenate $Na_2HAsO_4,12H_2O$ (the A.R. product is obtainable from the Mallinckrodt Chemical Works, U.S.A.; see Appendix, Section **A, 9**) in 100 ml. of water.

2. The **magnesia mixture** is *prepared* as follows. Dissolve 25 g. of magnesium chloride $MgCl_2,6H_2O$ and 50 g. of ammonium chloride in 250 ml. of water. Add a slight excess of ammonia solution, allow to stand overnight, and filter if a precipitate is present. Acidify with dilute hydrochloric acid, add 2 ml. excess of concentrated hydrochloric acid, and dilute to 500 ml.

3. The best results are obtained by conducting the final ignition in an electrically-heated muffle furnace at 800° to 900°C.

4. The following procedure (J. Dick, 1933) permits of the **weighing** as **magnesium ammonium arsenate** $MgNH_4AsO_4,6H_2O$. Treat the concentrated arsenate solution with 3 to 5 g. of ammonium chloride and 10 to 15 ml. of magnesia mixture. Add hydrochloric acid dropwise until the precipitate which has formed is dissolved. Add 1 drop of phenolphthalein to the cold solution, stir, then enough 2·5 per cent ammonia solution to turn the solution red, followed by an amount of concentrated ammonia solution equal to one-third of the volume of the solution. At this stage the total volume of the solution should not exceed 60 to 70 ml. for each 0·1 g. of As present. Cool in ice water for 1 to 2 hours, filter through a weighed crucible* (sintered glass or porous porcelain), wash with 2·5 per cent ammonia solution, followed by 95 per cent alcohol (5 or 6 times), and small volumes anyhdrous ether (5 or 6 times). Dry in a vacuum desiccator for 10 minutes or to constant weight. Weigh as $MgNH_4AsO_4,6H_2O$, which contains 25·89 per cent arsenic.

C. Determination of arsenic by precipitation as ammonium uranyl arsenate and weighing as uranous uranate. *Procedure.* The solution (150 ml.) should contain about 0·06 g. of As as arsenate. Add 30 ml. of 4*N* ammonia solution, acidify with acetic acid, heat to boiling, and add 50 ml. (excess) of approximately 0·1*N* uranyl acetate solution. Allow to stand several hours, but preferably overnight; during this period the pale yellow granular precipitate will become coarser. Filter through a fine quantitative filter paper, wash free from soluble salts, and transfer the filter and precipitate to a weighed silica or, better, a Main-Smith crucible. *Heat in a fume chamber provided with a good draught* until all the carbon has burnt off —the arsenic is simultaneously volatilised. Moisten the residue with a few drops of concentrated nitric acid, and ignite to constant weight over an ordinary Bunsen burner. Weigh as U_3O_8.

IV, 21. ANTIMONY

Discussion. Antimony may be determined in the following forms:

A. Antimony trisulphide, Sb_2S_3. This method is of limited application since no other elements that are precipitable by hydrogen sulphide in acid solution can be present, and the sulphide must be dried and finally heated in an atmosphere of carbon dioxide at 280° to 300°C. Arsenic can be separated by removal by distillation as arsenic trichloride; tin can be removed by precipitation in the presence of oxalic and tartaric acids or of phosphoric acid.

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* Wash the crucible several times with alcohol (95 per cent), followed by anhydrous ether, wipe the outside, leave in a vacuum desiccator for 5 minutes and weigh.

B. Antimony tetroxide, Sb_2O_4. Instead of weighing the antimony as the trisulphide after the procedure described in *Method A*, the wet sulphide (or sulphide dried at 100°C) may be converted by controlled oxidation with fuming nitric acid into the higher oxide, and subsequently heated at 750° to 800°C, and weighed as Sb_2O_4. Since this process is an inconvenient one and the oxide is very easily reduced, it will not be described in detail.

C. Antimony pyrogallate, $Sb(C_6H_5O_4)$. Antimonious salts in the presence of tartrate ions may be quantitatively precipitated with a large excess of aqueous pyrogallol as the dense antimony pyrogallate. The method allows of a simple separation from arsenic; the latter element may be determined in the filtrate from the precipitation of antimony by direct treatment with hydrogen sulphide.

The volumetric methods described in Chapter III are simpler, quite as accurate and more rapid; they are therefore to be preferred.

A. Determination of antimony as trisulphide. *Procedure.* Quickly heat the solution of the antimony compound in 1 : 4 hydrochloric acid (100 ml.) (1) contained in a conical flask to boiling and immediately pass a rapid stream of washed hydrogen sulphide; maintain the solution at 90° to 100°C. Shake the flask gently at intervals after the sulphide has turned red, and keep the precipitate, as far as possible, below the surface of the solution. As the precipitate darkens in colour, reduce the gas stream. Continue the passage of gas until the precipitate is crystalline and black in colour (total time required for precipitation is 30 to 35 minutes). Dilute the solution with an equal volume of water, mix, and heat again whilst the gas is slowly passed into the suspension for some minutes. When the solution is clear, cool, and filter through a filter crucible (Gooch, sintered glass or porous porcelain) that has been heated at 280° to 300°C and weighed. Wash the precipitate a few times with water to remove acid, and then with alcohol; draw air through the crucible to dry the precipitate as far as possible. Place the crucible and contents in a wide glass tube passing through the centre of an air bath (Section **II, 12F**) or through an electrically-heated tube furnace. Heat for 2 hours at 100° to 130°C in a current of carbon dioxide (this will completely dry the precipitate), and then heat for a further 2 hours at 280° to 300°C (this process will convert any Sb_2S_5 present into Sb_2S_3 and will volatilise the sulphur). Cool in a slow stream of carbon dioxide, then place in a desiccator for 20 to 30 minutes, and weigh as Sb_2S_3.

Note. 1. A solution, suitable for practice in this determination, may be prepared by dissolving 0·5 g., accurately weighed, of A.R. anhydrous potassium antimonyl tartrate or of pure tartar emetic in 150 ml. of 1 : 4 hydrochloric acid.

C. Determination of antimony as antimonious pyrogallate. *Procedure.* The solution should contain the antimony (0·1 to 0·2 g.) in the antimonious condition. Add a slight excess over the calculated quantity of Rochelle salt (sodium potassium tartrate) to avoid the formation of basic salts upon dilution. Dissolve approximately five times the theoretical quantity of pure pyrogallol (Section **I, 62, O**) in 100 ml. of air-free water, add this all at once to the antimony solution, and dilute to 250 ml. After 30 to 60 seconds the clear mixture becomes turbid, and then a dense cloudy precipitate forms which separates out rapidly. Allow to stand for 2 hours, filter through a weighed sintered glass or porous porcelain crucible, wash several times with cold water to remove the excess of pyrogallol (50 ml. is usually sufficient), dry at 100° to 105°C to steady weight. Wash again with cold water, dry at 100° to 105°C and weigh ; repeat the operation until the weight is constant. Weigh as $Sb(C_6H_5O_4)$.

IV, 22. TIN

Discussion. Tin may be determined in any of the following ways :

A. Tin dioxide, SnO_2. The method depends upon the oxidation of the tin to the quadrivalent state, precipitation with ammonium hydroxide, followed by ignition to stannic oxide, SnO_2. This procedure is satisfactory when applied to solutions containing tin alone, but it cannot be used directly in the presence of many other elements.

Tin is, however, frequently estimated as the dioxide in alloys (*e.g.*, in brass or gun metal). The alloy is treated with nitric acid, when a precipitate of hydrous stannic oxide is formed ; the formula for this may be written, for simplicity, as H_2SnO_3, metastannic acid :

$$3Sn + H_2O + 4HNO_3 = 3H_2SnO_3 + 4NO.$$

The precipitate possesses colloidal character and exhibits powerful adsorption properties for certain ions, for example, iron, lead, copper, nickel and zinc. It is advisable to use macerated filter paper in the subsequent filtration and also to wash the precipitate with dilute nitric acid in order to avoid peptisation. The precipitate is ignited at the highest temperature of a Méker type burner to stannic oxide :

$$H_2SnO_3 = SnO_2 + H_2O.$$

Owing to the ready reduction of the oxide to the metal, the carbon of the filter paper must be burnt off at as a low a temperature as possible and the flame gases excluded from the crucible.

The precipitate should be white, but rarely is because of the presence of impurities. The amount of impurity may be determined by adding to the impure weighed oxide 15 times its weight of pure ammonium iodide and heating for 15 minutes at 425° to 475°C, or until no further fumes are evolved (E. R. Caley and M. G. Burford, 1936). The tin is volatilised quantitatively as stannic iodide:

$$SnO_2 + 4NH_4I = SnI_4 + 4NH_3 + 2H_2O.$$

The residue is treated with 2 to 3 ml. of concentrated nitric acid, cautiously evaporated, ignited, and the residual metallic oxides weighed; the loss in weight gives the weight of pure stannic oxide present in the precipitate. The treatment with nitric acid is necessary, for the other metals are converted into iodides and/or oxyiodides, which are only slowly converted into the oxides by heating in air.

B. Precipitation with cupferron and weighing as stannic oxide, SnO_2. This process permits of the precipitation of tin in the presence of aluminium, chromium, cobalt, nickel and manganese. In the presence of 5 ml. of 48 per cent hydrofluoric acid per 200 to 400 ml. of solution, tin is not precipitated by hydrogen sulphide whereas copper, lead, tervalent arsenic and antimony are thus precipitated; many separations are therefore possible by this method.

C. Precipitation with phenylarsonic acid and weighing as stannic oxide, SnO_2. This method is applicable in the presence of zinc, copper, and other elements commonly associated with tin in alloys, etc. Zirconium and thorium seriously interfere and must be absent.

The volumetric methods described in Chapter III are more rapid and equally accurate; they are therefore generally preferred.

A. Determination of tin as dioxide. *Procedure.* Weigh out accurately 0·5 to 1·0 g. of the alloy (1) into a 150 ml. beaker covered with a clock glass or Fisher " speedvap " beaker cover. Add 15 ml. of concentrated nitric acid mixed with 10 ml. of water while keeping the beaker covered. When the vigorous action is over, evaporate the solution during a period of at least 1 hour on a water bath to a volume of 5 to 10 ml., but not to dryness. This digestion ensures the quantitative precipitation of the stannic acid. Dilute to about 50 ml., and heat on the water bath for 30 minutes (to dissolve soluble salts). Add a Whatman accelerator or one-quarter of a Whatman ashless tablet, and stir with the hot suspension for 5 minutes. Filter through a Whatman No. 42 or No. 542 filter paper into a 150 ml. beaker; if the first portion of the filtrate is not clear, pass it through a second time, and add more macerated filter paper if the precipitate persists in running through. Wash the precipitate at least 10 times with hot 1 per cent nitric acid. Fold up the filter, place it in a weighed porcelain crucible, dry and char the filter as at a low a temperature as possible, burn off the carbon at a very low red heat to avoid reduction, and finally ignite the residue for 30 minutes at the full heat of a Méker type of burner whilst keeping the crucible in a standing position, preferably in an asbestos or " uralite " shield, to permit the free access of air. (If reduction occurs, the precipitate may be moistened with a drop or two of nitric acid and ignited again.) Allow to cool in a desiccator and weigh. Repeat the ignition, etc., until constant weight is attained. Weigh as SnO_2.

If the residue is appreciably coloured, the amount of impurities may be determined as described in the *Discussion.*

Note. 1. Ridsdale's " Gun Metal, No. 6b " (one of the Analysed Samples for Students) is suitable. Alternatively 0·15 to 0·2 g. of A.R. tin may be used.

B. Determination of tin with cupferron. *Procedure.* Remove metals like copper, lead, tervalent arsenic and antimony, if present, by precipitation with hydrogen sulphide in the presence of hydrofluoric acid (see *Discussion*), and boil off the excess of hydrogen sulphide. The solution should contain 0·1 to 0·3 g. of Sn and occupy a volume of 200 to 500 ml. Add 5 to 10 ml. of concentrated hydrochloric acid, 4 g. of boric acid, 2 to 5 ml. of concentrated sulphuric acid, followed, whilst stirring, with a liberal excess of filtered 10 per cent aqueous cupferron solution. Stir vigorously for 30 to 45 minutes. The tin complex first separates in a white form (? emulsion), rapidly assumes a curdy appearance, passes through a stage when it resembles plastic sulphur, and finally becomes compact and brittle, and may be crushed to a fine powder with a glass rod. Filter upon a Whatman No. 41 or No. 541 filter paper, wash with cold water, dry in a weighed crucible, expel the organic matter by gentle ignition, and then ignite to constant weight. Weigh as SnO_2.

C. Determination of tin with phenylarsonic acid, $C_6H_5AsO(OH)_2$. *Procedure.* Treat a weight of the sample containing about 0·1 g. of Sn (1) with 10 ml. of 1 : 1 nitric acid, heat *gently* to complete oxidation and until excess of nitric acid has been removed ; take care not to dehydrate the metastannic acid. Add concentrated hydrochloric acid dropwise until complete solution is just obtained, dilute to 150 to 200 ml. with water, and adjust the acidity to 5 per cent of hydrochloric acid by volume (2). Heat the solution, and add 35 ml. of a saturated aqueous solution of phenylarsonic acid (3). Allow to stand several hours, and filter through a quantitative filter paper (4). Wash the precipitate with 4 per cent ammonium nitrate solution until free from chlorides (or sulphates). Ignite the precipitate and paper in a weighed crucible over a small flame until all the carbon is burnt off, and then heat in an electric furnace at 1075° to 1100°C to constant weight (5). Weigh as SnO_2.

Notes. 1. For practice in this determination, the student may use either A.R. tin or Ridsdale's " Brass, No. 5b " or " Gunmetal, No. 6b."

2. If bismuth is absent, sulphuric acid (7·5 per cent by volume) may be used.

3. The saturated aqueous solution is approximately 10 per cent.

4. The addition of a little macerated filter paper (Section **II, 29**) aids the filtration.

5. If an electric furnace is not available, a Méker or Fisher high temperature burner may be used.

IV, 23. MOLYBDENUM

Discussion. Molybdenum may be determined in the following forms :

A. Lead molybdate, $PbMoO_4$. Precipitation as lead molybdate is usually made by the slow addition of a solution of lead acetate to a hot dilute acetic acid-ammonium acetate solution containing the molybdenum. The method is applicable in the presence of copper, mercury, cobalt, nickel, manganese, zinc and magnesium. Alkali salts are not objectionable except sulphates, which must be absent when the alkaline earths are present. A great excess of the precipitant should be avoided if chlorides are present. Free mineral acids prevent complete precipitation, and elements such as iron, chromium, vanadium, tungsten, silicon, tin and titanium interfere.

B. Precipitation with α-benzoinoxime and weighing as molybdic oxide, MoO_3. Precipitation as the α-benzoinoxime complex is made by the addition of excess of an alcoholic solution of the reagent to a solution of the molybdenum compound containing 5 per cent by volume of sulphuric acid. The precipitate cannot be weighed as such, but must be ignited to molybdic oxide. The only other elements that give precipitates in mineral acid solution with the reagent are tungsten, palladium, sexivalent chromium, quinquevalent vanadium and tantalum. Chromium and vanadium do not interfere if they are reduced to the tervalent and quadrivalent states respectively with sulphurous acid. Tungsten may be determined in the ignited precipitate by extracting with the minimum volume of warm 1 : 3 ammonia solution, filtering, acidifying the ammoniacal solution with hydrochloric acid, and then adding a little cinchonine solution ; the solution is allowed to stand overnight, the precipitate filtered off, washed, ignited at 525°C, and weighed. The weight of ungstic oxide is deducted from that of the molybdic oxide.

C. Molybdenum "oxinate," $MoO_2(C_9H_6ON)_2$. Molybdates yield sparingly orange-yellow molybdyl "oxinate" with oxine solution; the *p*H of the solution should be between the limits 3·3 to 7·6. The complex differs from other "oxinates" in being insoluble in organic solvents and in many concentrated inorganic acids. The freshly precipitated compound dissolves only in concentrated sulphuric acid and in hot solutions of caustic alkalis. This determination is of particular interest as it allows a complete separation of molybdenum and rhenium.

For the **volumetric determination of molybdenum,** the precipitate is brought into solution by repeated digestion with 2 to 4*N* sodium hydroxide solution, the alkaline solution is slowly introduced with constant stirring into 25 to 50 ml. of concentrated hydrochloric acid; the solution diluted to 50 to 100 ml., and then titrated with standard 0·1*N* potassium bromate (Section **III, 138**; *Procedure A*).

1 Ml. N $KBrO_3$ = 0·01199 g. Mo.

A. Determination of molybdenum as lead molybdate. *Procedure.* Weigh out accurately about 0·4 g. of ferromolybdenum (1), dissolve it in 10 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid, evaporate to 2 to 3 ml., dilute to 50 ml., and transfer to a separating funnel. Dissolve 5 g. of sodium hydroxide in 200 ml. of water in the original beaker, heat to boiling, and run in the solution from the separating funnel dropwise and with constant stirring. Rinse out the funnel twice with boiling water, and add the washings to the main filtrate. Filter off the precipitated ferric hydroxide and wash with hot water. Dissolve the precipitate in the minimum volume of dilute hydrochloric acid, and reprecipitate by slowly pouring into a solution of about 4 g. of sodium hydroxide in 100 ml. of water. Filter off the precipitate, wash with hot water, and add the filtrate and washings to the main filtrate. Acidify with acetic acid, add 50 ml. of a 50 per cent solution of ammonium acetate, and make up to 500 ml. in a measuring flask. Remove 250 ml. of the solution (2), heat to boiling, and maintain near the boiling point with a small flame; add from a burette a solution of lead acetate (containing 4 g. of the salt and 1 ml. of glacial acetic acid per 100 ml.) dropwise and with constant stirring. When a slight excess of the precipitant has been added, the milky solution clears appreciably. When this occurs, boil for 2 to 3 minutes whilst the solution is stirred, allow to settle, and add a few drops of the reagent to see if precipitation is complete. A large excess of precipitant should be avoided. Digest on the steam bath for 15 to 30 minutes. Decant the clear solution through a weighed Gooch or porous porcelain crucible, wash by decantation 3 or 4 times with 75 ml. portions of hot 2 to 3 per cent ammonium nitrate solution, transfer the precipitate to the filter, and wash until the soluble salts have been removed. Dry and ignite the precipitate at a *dull* red heat as described in Section **IV, 14C.** Weigh as $PbMoO_4$.

Notes. 1. The Bureau of Analysed Samples " Ferro-Molybdenum, No. 200 " (a British Chemical Standard) is suitable.

2. If molybdenum is being determined in a simple salt, *e.g.*, in A.R. molybdic acid or molybdic anhydride, commence at this point. The solution should contain about 0·1 g. of Mo in 200 ml. and may be prepared as follows. Dissolve 0·15 g., accurately weighed, of A.R. molybdic acid or anhydride, in 50 ml. of dilute ammonia solution, acidify with acetic acid, add 25 ml. of a 50 per cent solution of ammonium acetate, and dilute to 200 ml.

B. Determination of molybdenum with α-benzoinoxime (cupron). *Procedure.* Prepare a solution containing 10 ml. of concentrated sulphuric acid in a volume of 200 ml. and not more than 0·15 g. of sexivalent molybdenum. If vanadates or chromates are present, add sufficient of freshly prepared sulphurous acid to reduce them, and heat to boiling: continue the boiling until the odour of sulphur dioxide can no longer be detected. Cool to 5° to 10°C, stir, and slowly add 10 ml. of a solution of the reagent (2 g. of α-benzoinoxime in 100 ml. of alcohol) and 5 ml. extra for each 0·01 g. of Mo present (from 2 to 5 times the theoretical amount is required). Continue the stirring, add just sufficient bromine water to tint the solution a pale yellow, and then add a few ml. of the reagent. Allow the mixture to stand for 10 to 15 minutes at 10° to 15°C with occasional stirring, and filter through a Whatman No. 40 or 540 filter paper. Wash the precipitate with 200 ml. of a cold, freshly-prepared wash solution (containing 10 ml. of the reagent, 2 ml. of concentrated sulphuric acid diluted to 200 ml.). Transfer the paper and washed precipitate to a weighed platinum crucible, char the paper at a low temperature without inflaming, and then ignite to constant weight at 500° to 525° C. Weigh as MoO_3.

C. Determination of molybdenum with oxine. *Procedure.* Neutralise the solution of alkali molybdate, containing up to 0·1 g. of Mo, to methyl red, and then acidify with a few drops of 2*N* sulphuric acid. Add 5 ml. of 2*N* ammonium acetate, dilute to 50 to 100 ml., and heat to boiling. Precipitate the molybdenum by the addition of a 3 per cent solution of oxine in dilute acetic acid (for preparation, see Section **IV, 37B**; Note 2) until the supernatant liquid becomes perceptibly yellow. Boil gently and stir for 3 minutes, filter through a filter crucible (sintered glass or porous porcelain), wash with hot water until free from the reagent, and dry to constant weight at 130° to 140°C. Weigh as $MoO_2(C_9H_6ON)_2$.

IV, 24. SELENIUM AND TELLURIUM

Discussion. The gravimetric estimation depends upon the separation and weighing as elementary selenium or tellurium (or as tellurium dioxide). Alkali selenites and selenious acid are reduced in hydrochloric acid solution with sulphur dioxide, hydroxylamine hydrochloride, and hydrazine sulphate or hydrate. Alkali selenates and selenic acid are not reduced by sulphur dioxide (they must first be reduced to selenious acid by prolonged heating with concentrated hydrochloric acid *under reflux*), but are readily reduced by hydrazine sulphate or hydrate. In working with selenium it must be remembered that appreciable amounts of the element may be lost on warming strong hydrochloric acid solutions of its compounds : no appreciable loss occurs if dilute acid solutions are heated at temperatures below 100°C.

With tellurium, precipitation of the element with sulphur dioxide is slow in dilute hydrochloric acid solution and does not take place at all in the presence of excess of acid ; moreover, the precipitated element is so finely-divided that it oxidises readily in the subsequent washing process. Satisfactory results are obtained by the use of a mixture of sulphur dioxide and hydrazine hydrochloride as the reducing agent, and the method is applicable to both tellurites and tellurates. Another method (B. S. Evans, 1933) utilises excess of sodium hypophosphite in the presence of dilute sulphuric acid as the reducing agent.

Two processes for the gravimetric estimation of mixtures of selenium and tellurium are described. Selenium and tellurium occur in practice either as the impure elements or as selenides or tellurides. They may be brought into solution by mixing intimately with 2 parts of sodium carbonate and 1 part of potassium nitrate in a nickel crucible, covering with a layer of the mixture, and then heating gradually to fusion. The cold melt is extracted with water, and filtered. The elements are then determined in the filtrate.

1. Determination of selenium. *Procedure A*. The selenium must be present in the quadrivalent state and the selenium content of the solution must not exceed 0·25 g. per 150 ml. Saturate the cool (15° to 20°C) selenium solution containing at least 28 per cent by volume of hydrochloric acid (3·4*N*) with sulphur dioxide, allow to stand until the red selenium subsides, filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash well successively with cold concentrated hydrochloric acid, cold water until free from chloride, alcohol, and ether. Dry the precipitate for 3 to 4 hours at 30° to 40°C to remove ether, and then to constant weight at 120° to 130°C. Weigh as Se.

Note. A simpler method (J. Dick, 1930) of drying and weighing the precipitated selenium, is to treat the well-washed precipitate, collected in a sintered glass or porous porcelain crucible, 5 or 6 times with small volumes of rectified spirit and then similarly with anhydrous ether. The precipitate is sucked dry at the pump for 10 minutes, the crucible wiped with a clean linen cloth, left in a vacuum desiccator for 10 minutes, and weighed.

Procedure B. The selenium may be present in either the quadrivalent or sexivalent state. Dissolve the substance containing not more than 0·3 g. of Se in 40 ml. of cold concentrated hydrochloric acid, and dilute to 100 ml. Add 10 ml. of a 25 per cent aqueous solution of hydroxylamine hydrochloride, and heat at 90°C for 4 hours. Transfer the black precipitate to a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash with water, then with alcohol, and dry at 110°C to constant weight.* Weigh as Se.

2. Determination of tellurium. *Procedure A.* The solution should contain not more than 0·2 g. of Te in 50 ml. of 3*N* hydrochloric acid (*ca.* 25 per cent by volume of hydrochloric acid). Heat to boiling, add 15 ml. of a freshly-prepared, saturated solution of sulphur dioxide, then 10 ml. of a 15 per cent aqueous solution of hydrazine hydrochloride, and finally 25 ml. more of the saturated solution of sulphur dioxide. Boil until the precipitate settles in an easily filterable form ; this should require not more than 5 minutes. Allow to settle, filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), and immediately wash with hot water until free from chloride. Finally wash with alcohol (to remove all water and prevent oxidation), and dry to constant weight at 105°C.* Weigh as Te.

In the alternative method of reduction, which is particularly valuable for the determination of small amounts of tellurium, the procedure is as follows. Treat the solution containing, say, up to about 0·01 g. of Te in 90 ml. with 10 ml. of 1 : 3 sulphuric acid, then add 10 g. of sodium hypophosphite, and heat on a steam bath for 3 hours. Collect and weigh the precipitated tellurium as above.

Procedure B. Dissolve the material (elementary tellurium, oxides or tellurites) in concentrated hydrochloric acid or in 10 per cent potassium hydroxide solution, using 2 ml. per 0·2 g. of oxide. If alkaline, just acidify the solution with hydrochloric acid, and dilute to 200 ml. with boiling water. Add a slight excess of dilute ammonia solution, and just acidify with acetic acid. Allow to cool, when the crystalline dioxide will separate out. Collect the precipitate on a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash with hot water, and dry at 105°C to constant weight. Weigh as TeO_2.

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* Alternatively use the rectified spirit—anhydrous ether method given in **Note** to **1.**

3. Determination of mixtures of selenium and tellurium. *Procedure A.* Dissolve the mixed oxides (not exceeding 0·25 g. of each) in 100 ml. of concentrated hydrochloric acid, and add with constant stirring 50 ml. of cool concentrated hydrochloric acid which has been saturated with sulphur dioxide at the ordinary temperature. Allow the solution to stand until the *red* selenium has settled, filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), and complete the determination as described in **1,** *Procedure A.* Preserve the filtrate, hydrochloric acid and water washings. Concentrate the latter on a water bath below 100°C (above 100°C tellurium is lost as chloride) to 50 ml., and estimate the tellurium as described under **2,** *Procedure A.*

Procedure B. Dissolve the mixed oxides (not exceeding 0·25 g. of each) in 40 ml. of concentrated hydrochloric acid. Add 10 ml. of 25 per cent hydroxylamine hydrochloride, and heat at 90°C for 4 hours. Filter off the *black* selenium through a weighed filter crucible, wash with water, then with alcohol, and dry to constant weight at 110°C. Determine the tellurium in the filtrate exactly as detailed in **2,** *Procedure A.*

IV, 25. PLATINUM

Discussion. Platinum may be determined in either of the following forms :

A. Metallic platinum. The platinum solution is treated with formic acid, best at *p*H 6, and the precipitated platinum weighed.

B. Ammonium chloroplatinate, $(NH_4)_2[PtCl_6]$, and subsequent weighing as platinum. If platinum alone is present in hydrochloric acid solution, it may be precipitated as ammonium chloroplatinate by the addition of a half-saturated solution of ammonium chloride, washed, carefully ignited, and weighed at Pt.

A. Determination as metallic platinum. *Procedure.* In this estimation any excess of nitric and/or hydrochloric acid present must be removed. Evaporate the solution of platinum, containing no other platinum metals (ruthenium, rhodium, palladium, osmium, and iridium) and gold, to a syrup on the steam bath so as to remove as much hydrochloric acid as possible. If nitric acid was present, dissolve the residue in 5 ml. of water, heat on the water bath for a few minutes, add 5 ml. of concentrated hydrochloric acid, and again evaporate to a syrupy consistency. Dissolve the residue in water, and dilute so that the solution does not contain more than 0·5 g. of Pt. in 100 ml. For each 100 ml. of solution, add 3 g. of anhydrous sodium acetate and 1 ml. of formic acid. Heat on the boiling water bath for several hours. Filter through a quantitative filter paper. Add a little more sodium acetate and formic acid to the filtrate and digest in order to ensure complete precipitation. Wash the precipitate with water until free from chloride, dry and ignite the filter paper in contact with the precipitate (Section **II, 36A**) to constant weight. Weigh as metallic Pt.

B. Determination of platinum by precipitation as ammonium chloroplatinate. *Procedure.* Only hydrochloric acid may be present in this estimation. The solution should be free from gold (which may be removed by the cautious addition of sulphurous acid to the solution or of hydroquinone to the solution 1·2*N* with respect to hydrochloric acid) and the other platinum metals (see, however, below). If nitric acid is present, it must be removed by several evaporations with concentrated hydrochloric acid. Dissolve the residue in 5 ml. of concentrated hydrochloric acid and 20 ml. of hot water, and then add gradually an equal bulk of half-saturated ammonium chloride solution. Allow to stand for some hours or overnight. Filter off the precipitate, wash it with the ammonium chloride solution, and finally twice with cold water. Transfer the filter paper and precipitate to a Main-Smith crucible (Section **II, 36B**), heat extremely slowly at first (otherwise loss may occur), and ultimately raise to a strong red heat. Heat to constant weight and weigh as Pt.

If other metals of the platinum group are present, the above procedure does not give satisfactory results. It is necessary to proceed as follows. Rinse back the precipitate of ammonium chloroplatinate into the precipitating vessel, and wash the filter thoroughly with hot water. Slightly acidify the liquid (150 ml. for 1 g. of Pt) with hydrochloric acid, boil vigorously and keep stirred by means of a glass tube through which a brisk current of chlorine is passed (the operation must be performed in the fume chamber). When the precipitate has dissolved (after a few minutes), stop the current of chlorine, and wash the tube with hot water. The solution now contains chloroplatinic acid. Then add just enough ammonium chloride solution to combine with the platinum (6 ml. of a 10 per cent solution for 1 g. of platinum), and evaporate (hot plate) to 20 ml. Allow to cool, and dilute with an equal bulk of saturated ammonium chloride solution. After a few hours, filter off the coarsely crystalline precipitate, wash with half-saturated ammonium chloride solution, then with a little cold water, ignite cautiously, and weigh as Pt.

IV, 26. PALLADIUM

Discussion. Palladium may be determined in one of the following forms :

A. Palladous cyanide, $Pd(CN)_2$, and subsequent weighing as the metal. This is quite a good method particularly when large quantities of palladium are involved, because of the comparative compactness of the precipitate.

B. Palladium dimethylglyoxime, $Pd(C_4H_7N_2O_2)_2$. This is one of the best methods for the estimation of the element. Gold must be absent for it precipitates as the metal even from cold solutions. The other platinum metals do not, in general, interfere. Moderate amounts of platinum cause little contamination of the precipitate, but with large amounts a second precipitation is desirable. The precipitate is decomposed by digestion on the water bath with a little aqua regia, and diluted with an equal volume of water ; the resulting solution is largely diluted with water, and the palladium reprecipitated with dimethylglyoxime.

An objection to the precipitation of palladium with dimethylglyoxime is the voluminous character of the precipitate. Hence if much palladium is present, an aliquot part of the solution should be used, or the palladous cyanide method applied.

C. Palladium α-nitroso-β-naphtholate $Pd(C_{10}H_6O_2N)_2$. α-Nitroso-β-naphthol was first employed for the determination of palladium by precipitating with this reagent and subsequently igniting the slightly contaminated complex to, and weighing as, the metal. If the hydrogen peroxide-sodium hydroxide method is employed (compare Cobalt, Section **IV, 33A**), the precipitate has the composition $Pd(C_{10}H_6O_2N)_2$ and may be weighed in this form after drying at 135°C. The method may be employed to separate palladium from platinum.

D. Palladium α-nitro-β-naphtholate $Pd(C_{10}H_6O_3N)_2$. α-Nitro-β-naphthol behaves similarly to α-nitroso-β-naphthol, but is stable in aqueous solution. The precipitate is of definite composition, $Pd(C_{10}H_6O_3N_2)_2$, and may be weighed after drying at 130° to 135° C. The procedure provides a method of separation from platinum.

A. Determination of palladium as palladous cyanide. *Procedure.* This estimation must be carried out in a fume cupboard provided with a good draught. Nearly neutralise the solution containing up to 0·3 g. of Pd with sodium carbonate, and add an excess of mercuric cyanide solution. Heat on the water bath until the odour of hydrocyanic acid has disappeared, and allow the light yellow precipitate to settle. Filter the precipitate through a quantitative filter paper. Wash the precipitate first by decantation and then on the filter with cold water. Dry and ignite in a weighed crucible to constant weight using the full heat of a Méker type of burner. Weigh as Pd.

B. Determination of palladium with dimethylglyoxime. *Procedure.* The solution should contain not more than 0·1 g. of Pd in 250 ml., be 0·25*N* with respect to hydrochloric or nitric acid, and be free from nickel and gold. Add, at room temperature, a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol. Use 2 to 5 ml. of the reagent for every 10 mg. of palladium. Allow the solution to stand for 1 hour, and then filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain). Test the filtrate with a little of the reagent to make sure that precipitation is complete. Wash the orange-yellow precipitate of palladium dimethylglyoxime thoroughly, first with cold water and then with hot water. Dry at 110°C to constant weight. Weigh as $Pd(C_4H_7O_2N_2)_2$.

C. Determination of palladium with α-nitroso-β-naphthol. *Procedure.* The solution should have a volume of about 20 ml. and contain about 0·03 g. of Pd. Treat the solution with 10 drops of 100-volume hydrogen peroxide, followed by 2*N* sodium hydroxide until alkaline : cover the beaker with a clock glass until the evolution of oxygen subsides. Add 30 ml. of glacial acetic acid, dilute to 150 ml., heat to boiling, and precipitate with 15 ml. of the 1 per cent reagent solution (for the preparation of the 2 per cent solution, see Section **I, 62G**). Filter the reddish-brown flocculent precipitate through a weighed sintered glass or porous porcelain crucible, wash 3 times with 20 per cent acetic acid, and finally with boiling water until the washings are colourless. Dry to constant weight at 135°C. Weigh as $Pd(C_{10}H_6O_2N)_2$.

D. Determination of palladium with α-nitro-β-naphthol. *Procedure.* The palladium solution should have a volume of about 20 ml. and contain not more than 0·03 g. of Pd. Add 10 drops of 100-volume hydrogen peroxide followed by 2*N* sodium hydroxide until alkaline ; cover the beaker with a clock glass for oxygen is evolved. Dissolve the precipitate in glacial acetic acid and dilute so that the solution contains at most 5 per cent of acetic acid : a higher concentration of acetic acid exerts a solvent action upon the precipitate. Precipitate with 15 ml. of the reagent (for preparation, see Section **I, 62H**). Filter through a weighed sintered glass or porous porcelain crucible, wash three times with 5 per cent acetic acid, and finally with hot water. Dry to constant weight at 130° to 135°C. Weigh as $Pd(C_{10}H_6O_3N)_2$.

IV, 27. GOLD

Discussion. Gold is nearly always determined as the metal. The reducing agents which were generally employed are sulphur dioxide, oxalic acid and ferrous sulphate. No free nitric acid must be present in the solution ; if this is the case, the nitric acid must be removed by repeated evaporation with concentrated hydrochloric acid, and the solution diluted with water. With sulphurous acid, small amounts of the platinum metals (particularly platinum) may be carried down with the precipitate. It is therefore usually necessary to redissolve the solid in dilute aqua regia and to reprecipitate the gold ; oxalic acid gives a better separation from the platinum metals in the second precipitation, although the precipitate is somewhat finely divided. Ferrous sulphate gives satisfactory results for gold alone, but difficulties are introduced if the platinum metals are subsequently to be determined.

The best results are obtained with hydroquinone as the reducing agent (F. E. Beamish, J. J. Russell, and J. Seath, 1937). Precipitation in hot 1·2*N* hydrochloric acid solution is rapid, the gold is readily filtered, and occlusion of the platinum metals is negligible. Precipitation in the cold is complete in 2 hours. Palladium in the filtrate can be precipitated directly with dimethyl-glyoxime, whilst platinum in the filtrate may be determined by evaporating to dryness in order to destroy organic matter and then digesting with a little aqua regia.

Gold may also be separated from hydrochloric acid solutions of the platinum metals by extraction with ether or with ethyl acetate (compare Section **I, 71**) ; except in special cases these methods do not offer any special advantages over the reduction to the metal.

Determination of gold as the metal. *Procedure A.* The solution should contain not more than 5 ml. of concentrated hydrochloric acid per 100 ml. of solution, not more than 0·5 to 1 g. of Au, and be free from lead, selenium, tellurium, and the alkaline earths. Add 25 ml. of a freshly prepared saturated sulphur dioxide solution, and digest for 1 hour on the steam bath in order to coagulate the precipitate. Add 5 to 10 ml. more of the sulphur dioxide solution, and allow to cool. If the cold solution smells strongly of sulphur dioxide, the precipitation of gold is complete. Some of the metal is finely divided, and it is therefore advisable to treat the filter paper with a suspension of macerated filter paper prepared from a Whatman accelerator or ashless tablet. Pour the supernatant liquid through a Whatman No. 42 or No. 542 filter paper, preferably containing some filter paper pulp, and transfer as little as possible of the precipitate to the paper unless one precipitation is thought sufficient ; this will only be the case if very small amounts of platinum or palladium are present. Wash well by decantation with hot dilute hydrochloric acid (1 : 99). Transfer the filter to the beaker, and redissolve the gold in dilute aqua regia ; use 8 ml. of concentrated hydrochloric acid, 2 ml. of concentrated nitric acid and 10 ml. of water for each gram or less of gold. Filter from the paper pulp, and wash thoroughly with hot dilute hydrochloric acid (1 : 99). Evaporate the filtrate to dryness on the water bath, add 2 to 3 ml. of concentrated hydrochloric acid, and evaporate to dryness again ; repeat this operation twice in order to eliminate all the nitric acid. Treat the residue with 3 ml. of concentrated hydrochloric acid, 5 drops of concentrated sulphuric acid and 75 ml. of water, disregard the small amount of gold which may separate, add 25 ml. of a saturated solution of oxalic acid, and boil for a minute or two. If no further visible precipitation of gold occurs, digest the solution on the water bath for at least 4 hours. Filter off the gold through a filter paper (as described above), and wipe the inside of the beaker with small pieces of quantitative filter paper to ensure that all the metal is transferred from the beaker ; wash well with 1 : 99 hydrochloric acid. Transfer the filter to a weighed porcelain or silica crucible, burn off the paper carefully, and ignite to constant weight. Weigh as Au.

Procedure B. Treat the dilute solution of the gold, containing only a little free hydrochloric acid, with a large excess of a clear ferrous sulphate solution, cover the beaker, and heat on the water bath for several hours. Filter off the precipitated gold through a filter paper, and complete the estimation as under *Procedure A*.

Procedure C. The solution must be free from nitric acid, be about 1·2*N* with respect to hydrochloric acid (*ca.* 5 ml. of concentrated hydrochloric acid in 50 ml. of water), and contain up to 0·2 g. of Au in 50 ml. Heat the solution to boiling, add excess of 5 per cent aqueous hydroquinone solution (3 ml. for every 25 mg. of Au), and boil for 20 minutes. Allow to cool, and filter either through a weighed porous porcelain crucible (A2) or through a Whatman No. 42 or 542 filter paper (Section **II, 28**) ; wash thoroughly with hot water. The small particles of gold remaining in the bottom of the beaker (easily seen with a small flash lamp) are best removed with pieces of ashless filter paper. Ignite the porous porcelain crucible to constant weight. If filter paper is used, transfer to a weighed porcelain or silica crucible, and complete the estimation as described in *Procedure A*.

IV, 28. ALUMINIUM

Discussion. Aluminium may be determined in the following forms :

A. Aluminium oxide, Al_2O_3. Full details of this determination (precipitation with ammonia solution) are given in Section **IV, 9.** A more readily filterable precipitate may be obtained by precipitation in *weakly* acid solution with a mixture of equal volumes of a 25 per cent aqueous solution of potassium iodide and a saturated solution of potassium iodate. The mixture removes the acid produced by hydrolysis, and causes the reaction to proceed from left to right :

$$2AlCl_3 + 3H_2O \rightleftharpoons 2Al(OH)_3 + 6HCl \qquad \text{(i) ;}$$

$$6HCl + KIO_3 + 5KI = 3H_2O + 3I_2 + 6KCl.$$

The *weakly* acid solution (200 to 300 ml. containing up to 0·2 g. of Al) is treated with an excess of the KI-KIO_3 mixture ; iodine separates immediately. After 10 minutes the iodine is removed by the addition of sodium thiosulphate solution with stirring from a burette, and several ml. excess of the thiosulphate solution are added. The mixture is heated on a water bath for 45 minutes with frequent stirring. The hydrated aluminium oxide is filtered off, washed with hot water or with 2 per cent ammonium nitrate solution, ignited and weighed. The method may be applied also to the precipitation of chromium and iron as hydroxides from dilute, weakly acid solutions of their tervalent salts.

Sodium thiosulphate may also be employed to remove the acid formed by hydrolysis of the aluminium salt (equation (i)) :

$$6HCl + 3Na_2S_2O_3 = 3H_2O + 6NaCl + 3S + 3SO_2.$$

The mixture of aluminium hydroxide and sulphur, which is precipitated, can be readily filtered and washed. Here the dilute solution is neutralised with ammonium carbonate until a slight precipitate forms, which is dissolved in a little hydrochloric acid. Excess (say, 2 g.) of sodium thiosulphate dissolved in a small volume of water is added, the solution heated to boiling, and boiled until all traces of sulphur dioxide are expelled. 1 : 1 Ammonia solution is added until its odour is barely perceptible after blowing away the vapours, and the mixture boiled for 2 minutes. The precipitate is filtered off, washed, and ignited in the usual way.

Precipitation of aluminium hydroxide can also be brought about by bases other than ammonia, *e.g.*, phenylhydrazine, pyridine, aniline, etc. Of these *phenylhydrazine is sometimes employed for the separation of aluminium from divalent iron* in a form suitable for immediate ignition and weighing as the oxide. (Phenyl hydrazine also precipitates, best from solution of the sulphates, chromium, titanium, zirconium, and thorium ; beryllium is incompletely precipitated ; ceric and ferric salts are partially reduced and incompletely precipitated.) For the determination of aluminium the dilute sulphuric acid solution, free from elements of Group II and other interfering elements, is made slightly alkaline (methyl orange) with ammonium hydroxide solution, then just enough acid is added to hold the other elements in solution, and the solution is diluted to 100 to 200 ml. The whole is then heated, any iron present is reduced by the addition of a little saturated ammonium bisulphite solution, the solution quickly neutralised with ammonia solution, and 6 to 7 drops of 1 : 1 hydrochloric acid added. One to three ml. of pure phenylhydrazine is then added according to the amount of aluminium to be precipitated, followed by one Whatman " accelerator " ; the mixture is stirred until the precipitate becomes flaky, and is then allowed to settle. The supernatant liquid will be alkaline to methyl orange but acid to litmus. If the precipitate has a brownish colour, this is due to the colouring matter contained in the phenylhydrazine and not to ferric hydroxide. The precipitate is filtered after a short time, washed with a solution of phenylhydrazine sulphite,* and ignited to Al_2O_3 in the usual manner.

B. Basic aluminium succinate and subsequent ignition to the oxide, Al_2O_3. Aluminium can be precipitated as the dense basic succinate by boiling an acid solution containing succinic acid with urea (H. H. Willard and N. K. Tang, 1937). The hydrolysis of the urea forms ammonia gradually in a homogeneous solution, resulting in a *p*H of 4·2 to 4·6 :

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3.$$

The dense precipitate is easily filtered and washed, and exhibits much less tendency to adsorption of other salts than does the precipitate obtained by precipitation as the hydroxide. Upon ignition, the basic succinate is readily converted into alumina.

This method permits the separation of aluminium from large amounts of ferrous iron, nickel, cobalt, manganese, zinc, calcium, barium, and magnesium. For the separation of aluminium and iron, the latter must be maintained in the ferrous state by the addition of phenylhydrazine ; for zinc and aluminium, the precipitate contains a little zinc which can be removed by volatilisation at 1000° to 1100°C in a current of hydrogen introduced through a silica Rose crucible cover and inlet tube.

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* Prepared by adding a cold saturated solution of sulphurous acid to a few ml. of phenylhydrazine until the crystalline sulphite first formed dissolves in the excess, and then adding phenylhydrazine drop-wise and with vigorous shaking until the odour of sulphur dioxide is no longer perceptible. Use 5 to 10 ml. of this solution in 100 ml. of hot water.

C. Aluminium 8-hydroxy-quinolate, $Al(C_9H_6ON)_3$. Details of this method are given in Section **III, 138A.** This procedure separates aluminium from beryllium, the alkaline earths, and magnesium. For the gravimetric determination a 2 or 5 per cent solution of oxine in 2*N* acetic acid may be used ; 1 ml. of the latter solution is sufficient to precipitate 0·003 g. of Al. For practice in this determination, about 0·4 g. of A.R. ammonium alum, accurately weighed, may be used. This is dissolved in 100 ml. of water. The precipitated aluminium " oxinate " is collected on a weighed filter crucible (Gooch, sintered glass or porous porcelain), well washed with cold water, dried to constant weight at 110° to 120°C, and weighed as $Al(C_9H_6ON)_3$.

B. Determination of aluminium as the basic succinate and ignition to aluminium oxide. *Procedure.* The solution should contain about 0·1 g. of Al and be acid with hydrochloric acid. Add dilute ammonia solution until the solution becomes slightly turbid, remove the turbidity with dilute hydrochloric acid, and add 1 to 2 drops in excess. Add a solution of 5 g. of A.R. succinic acid in 100 ml. of water, followed by 10 g. of ammonium chloride and 4 g. of urea : dilute to 500 ml. with distilled water. Heat the solution to boiling and continue the boiling for 2 hours after the solution has become turbid (*ca.* 45 minutes).* Allow the precipitate to settle for a few minutes, add a Whatman " accelerator," filter, and wash 10 times with a 1 per cent succinic acid solution made neutral to methyl red with ammonia solution. If any precipitate adheres to the sides of the beaker, dissolve it in a little dilute hydrochloric acid, add a drop of methyl red or phenol red indicator, and then dilute ammonia solution until just alkaline ; filter off the precipitate of aluminium hydroxide on a separate small filter paper, and wash it with a 2 per cent solution of ammonium nitrate. Place both papers and precipitates in a silica or, preferably, a platinum crucible, and ignite to constant weight at 1200°C (compare Section **IV, 9**). Weigh as Al_2O_3.

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* The boiling period (after the appearance of a turbidity) may be reduced to 1 hour by first partially neutralising the hot solution to bromo-phenol blue or to methyl orange by the drop-wise addition of dilute ammonia solution : a very faint opalescence will appear.

IV, 29. BERYLLIUM

Discussion. Until about 1927 beryllium was nearly always determined by precipitation as the hydroxide $Be(OH)_2$ with ammonia solution in the presence of ammonium chloride or nitrate, and subsequently weighing as the oxide BeO. The method was not entirely satisfactory owing to the gelatinous nature of the precipitate, its tendency to adhere to the sides of the vessel, and its liability to adsorption and related effects. Beryllium hydroxide was usually separated with aluminium hydroxide, which it resembles in many respects; two methods for the separation of beryllium and aluminium are given below.

It has been shown (L. Moser, 1927) that the hydroxide may be obtained in an easily filterable and compact form by precipitation from neutral solutions by heating with ammonium nitrate and methyl alcohol at 70°C, a current of air being passed through the solution. This method provides a separation from all metals of the later analytical groups, excepting barium, which should previously be removed as sulphate; cadmium and thallium also do not interfere.

Beryllium may also be conveniently estimated by precipitation with tannin in ammoniacal solution. Elements such as aluminium, chromium, ferric iron, thorium, zirconium and titanium, are precipitated by tannin from acetic acid solution; beryllium is not precipitated under these conditions, hence a good method of separation from these elements is available. If ferric iron is present, slight reduction to the ferrous state occurs; this is prevented by the addition of a few drops of 10-volume hydrogen peroxide solution prior to precipitation with tannin.

Beryllium may also be quantitatively separated from aluminium by means of oxine.

In all these methods the element is weighed as beryllia, which is somewhat hygroscopic. The ignited residue must be cooled in a desiccator over concentrated sulphuric acid or phosphorus pentoxide, preferably in a tared and stoppered weighing bottle, and weighed as quickly as possible—usually after 25 minutes.

A. Determination of beryllium by precipitation with ammonia solution. *Procedure.* The beryllium solution (200 ml.), prepared with nitric acid or hydrochloric acid and containing about 0·1 g. of Be, must be almost neutral and contain no other substance precipitable by ammonia solution. Heat to boiling, and add dilute ammonia solution slowly and with constant stirring until present in *very slight* excess. Add a Whatman accelerator or one-half of a Whatman ashless tablet, boil for 1 or 2 minutes, and filter on a Whatman No. 41 or No. 541 filter paper. Transfer as much of the precipitate as possible by rinsing with hot 2 per cent ammonium nitrate solution. Remove any precipitate adhering to the walls of the beaker by dissolving in the minimum volume of hot very dilute nitric acid, heating to boiling, and precipitating as before. Filter through the same paper, and wash thoroughly with the ammonium nitrate solution. Place the paper and precipitate in a weighed silica, platinum, or Main-Smith crucible, dry, heat at a low temperature until the carbon has been destroyed, and finally ignite with a Méker type of burner (at approximately 1000°C). Allow to cool in a desiccator over concentrated sulphuric acid or phosphoric oxide, and weigh rapidly after 25 minutes. Repeat the ignition until constant weight is attained. Weigh as BeO.

A′. Determination of beryllium by hydrolysis with ammonium nitrite. *Procedure.* Neutralise the feebly acid solution, containing about 0·1 g. of BeO per 100 ml., cautiously with sodium carbonate, and remove the resultant slight opalescence with a few drops of dilute acid. Heat the solution to 70°C, pass a current of air through it, and add, with stirring, 50 ml. of 6 per cent ammonium nitrite solution and 20 ml. of methyl alcohol for each 0·1 g. of BeO expected to be present. Any acid-forming oxides of nitrogen are thus removed as methyl nitrite. The solution becomes cloudy after a few minutes. Complete the precipitation by boiling gently for 30 minutes. Add a further 10 ml. of methyl alcohol, and, after 10 minutes, filter through a Whatman No. 41 or No. 541 filter paper, wash thoroughly with hot water, dry, and ignite as in **A.** Weigh as BeO.

A″. Determination of beryllium by means of tannin. *Procedure.* The solution (300 to 400 ml.) should be weakly acid, free from all cations other than those of alkali metals, and contain at most 0·1 g. of BeO. Add 20 to 30 g. of ammonium nitrate, heat to boiling, and treat with 10 per cent aqueous tannin solution (use 10 times as much tannin as there is BeO present) with constant stirring, followed by ammonia solution, dropwise, until precipitation is complete. (the solution should be just basic to litmus paper). The precipitate is bulky but not gelatinous, is readily filtered, and shrinks to a relatively small volume on suction. Filter on a Whatman No. 40 or No. 540 filter paper resting upon a Whatman filter cone (hardened, No. 51), and apply suction. Wash with hot water. If alkali metals are present, wash the precipitate back into the beaker, dissolve in a little hydrochloric or sulphuric acid, and precipitate the boiling solution with ammonia solution as before. Filter, dry the paper and precipitate at 110° to 130°C, transfer to a weighed silica, platinum or Main-Smith crucible, ignite, add a few drops of concentrated nitric acid (to remove any organic matter which may be present), ignite strongly, allow to cool in a desiccator, and rapidly weigh as BeO.

B. Determination of beryllium in the presence of Al, Cr, Fe, Th and V by means of tannin. *Procedure.* The solution should be neutral, occupy a volume of 300 to 400 ml. (depending upon the amount of aluminium, etc., present, but this should not exceed 0·1 g.), and contain 30 to 40 g. of ammonium acetate, and 20 to 25 g. of ammonium nitrate. Treat with 15 to 20 ml. of 2*N* acetic acid, boil, and precipitate by the addition, with stirring, of excess of 10 per cent aqueous tannin solution or of a 3 per cent solution of tannin in saturated ammonium acetate solution. Filter the tannin adsorption-complex on a filter paper with suction as in **A″**, and wash with dilute ammonium nitrate solution. Rinse back the precipitate into the beaker by means of a stream of hot water from a wash bottle, and dissolve it by the addition of dilute sulphuric acid to the hot liquid. Nearly neutralise the resulting solution with ammonia solution, and repeat the precipitation as before with ammonium acetate, ammonium nitrate and acetic acid. After the precipitate has settled, decant the clear supernatant liquid through the filter used for the first filtration, wash the precipitate by decantation with hot ammonium nitrate solution, transfer it completely to the filter, and wash with the hot ammonium nitrate solution until the washings are sulphate-free (test with barium chloride and hydrochloric acid). Precipitate the beryllium in the filtrate and washings by the addition of more tannin solution (if necessary), followed by excess of ammonia solution. Complete the determination as in **A″**. Weigh as BeO.

If ferric iron is present, add a few drops of 10-volume hydrogen peroxide before precipitating with tannin solution to minimise the chance of any ferrous iron being formed.

If titanium and/or zirconium are present, precipitation may be effected in the presence of more concentrated acid because the tannin complexes of these metals are less soluble ; only one precipitation is necessary. The procedure is as follows. To the cold solution (300 ml.) add ammonia solution until it produces an incipient cloudiness, then add ammonium acetate (10 g.), ammonium nitrate (20 g.), and 80 per cent acetic acid (25 ml.). Heat the solution to boiling, and precipitate the titania and/or zirconia by the addition, with stirring, of 10 per cent aqueous tannin solution in ten-fold excess of the weight of the combined oxides. Boil for a few minutes, filter, wash the precipitate with 10 per cent acetic acid and a little ammonium nitrate. Determine the beryllium in the filtrate and washings as above.

Note. If any one of the above metals is present alone with the beryllium it may be determined by igniting the tannin complex, produced in acetic acid solution, to the oxide in the usual way.

B′. Determination of beryllium in the presence of aluminium by means of oxine. *Procedure.* Precipitate the aluminium from an ammonium acetate acetic acid solution (Section **IV, 28B**), and keep the filtrate. Heat the filtrate to boiling, and add a very slight excess of dilute ammonia solution. Filter off the precipitated beryllium hydroxide (preferably after the addition of macerated filter paper in the form of a Whatman accelerator or one-third of an ashless tablet), which is coloured yellow or brown by adsorbed oxine, through a Whatman No. 41 or No. 541 filter paper, wash thoroughly with a hot dilute solution of ammonium acetate containing a few drops of ammonia solution, and complete the determination as in **A.**

IV, 30. CHROMIUM

Discussion. Chromium may be determined in one of the following forms:

A. Chromic oxide, Cr_2O_3. The chromium must be present in solution as a chromic compound. It can be precipitated as the hydroxide exactly as described under Aluminium in Section **IV, 9** by means of the smallest possible excess of ammonia solution (the precipitate is appreciably soluble in excess of ammonia solution) in the presence of excess of ammonium salts. It is important to adjust the *p*H of the solution because of the amphoteric character of hydrated chromic oxide; the colour of the solution prevents the use of internal indicators so that electrometric methods must be used; however, the indicator (methyl red) may be used "externally."

The KI-KIO_3 method (Section **IV, 28**) gives a more easily filterable precipitate:

$$2CrCl_3 + 6H_2O \rightleftharpoons 2Cr(OH)_3 + 6HCl;$$
$$6HCl + 5KI + KIO_3 = 3H_2O + 3I_2 + 6KCl.$$

The best results are obtained by precipitation based upon the slow hydrolysis of potassium cyanate (Dorrington and A. M. Ward, 1930); this yields a granular precipitate of chromic hydroxide which is readily filtered and washed. This procedure will accordingly be described in detail.

A disadvantage of the chromic oxide method is that the results obtained are frequently a few tenths of a per cent too high on account of the formation of small amounts of chromic chromate, $Cr_2(CrO_4)_3$. For highly accurate results the precipitate should be ignited and allowed to cool in hydrogen.

B. Mercurous chromate, Hg_2CrO_4, and subsequent weighing as Cr_2O_3. The chromium must be present as chromate, and the solution should be free from chloride and large amounts of sulphate. Upon ignition, mercurous chromate is converted into chromic oxide. Numerous kations interfere, hence the method has a very limited application.

C. Barium chromate, $BaCrO_4$. The chromium must be present as chromate. The method is of limited application because of the general insolubility of chromates. Chlorides do not interfere, but sulphates must, of course, be absent. For further properties of barium chromate, see Section **IV, 45B.**

To convert a **chromic salt into a chromate,** treat the chromic solution contained in a porcelain dish with several ml. of bromine water, followed by freshly-prepared potassium hydroxide solution until alkaline. Warm until the odour of bromine disappears.

To convert a **chromate into a chromic salt,** acidify the solution with hydrochloric acid, and *either* add excess of freshly-prepared saturated sulphurous acid and boil until all the sulphur dioxide has been removed, *or* add concentrated hydrochloric acid and a little alcohol, and boil until the odour of acetaldehyde can no longer be detected and the solution is green. For practice in this operation, determination **A** may be carried out with A.R. potassium dichromate, previously dried at 180° to 200°C for 1 hour. 0·5 Gram of the salt is accurately weighed out into a 600 ml. beaker, dissolved in about 150 ml. of water, 5 ml. of concentrated hydrochloric acid and 15 ml. of alcohol added, and the whole heated until the solution is green and no longer smells of alcohol or of acetaldehyde. The solution is diluted to 300 ml., and the chromium precipitated as the hydroxide.

A. Determination of chromium as hydroxide by hydrolysis of potassium cyanate. *Procedure.* Weigh out accurately sufficient of the chromic salt to contain about 0·15 g. of Cr (1), and dissolve it in 200 ml. of cold water. Add 5 g. of ammonium chloride and 1 g. of potassium cyanate, and stir the solution until the solid has dissolved. Heat the solution *slowly* to boiling, when a fine granular precipitate separates gradually. Allow the precipitate to settle, decant the turbid liquor through a Whatman No. 41 or No. 541 filter paper (*a*), and wash the precipitate once by decantation with hot 2·5 per cent ammonium nitrate solution rendered faintly ammoniacal. Heat the filtrate to boiling, add a few drops of alizarin-S indicator (2) followed by concentrated hydrochloric acid until the solution is permanently yellow, and then add ammonia solution until the indicator is just red. Collect the small precipitate which is formed upon a separate filter (*b*), and wash it with hot ammonium nitrate solution. Wash the main bulk of the precipitate by decantation with ammonium nitrate solution, filter off on paper (*a*), and wash with the same solution. Dissolve the film of precipitate which adheres firmly to the beaker in a few drops of hydrochloric acid, reprecipitate it in the presence of alizarin-S by means of ammonia solution in very slight excess, and filter it upon the second filter (*b*). Ignite both filters in a weighed platinum crucible ; when the carbon has burnt off, ignite for 10 minutes at the maximum heat of a Méker type of burner, and weigh as Cr_2O_3.

Notes. 1. For practice, the student may employ about 2 g., accurately weighed, of A.R. chrome alum $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ for this estimation.

2. The alizarin-S indicator is prepared by dissolving 1 g. of the solid in 1 litre of water, and filtering from any insoluble matter present.

B. Determination of chromium by precipitation as mercurous chromate. *Procedure.* The solution (1) should be neutral or faintly acid, and contain about 0·1 g. of Cr as chromate (or dichromate) in 100 ml. To the cold solution add a decided excess of mercurous nitrate solution (2), whereby a brown amorphous precipitate of basic mercurous chromate is formed. Heat the solution to boiling, stirring frequently, until the precipitate is converted into the bright red and crystalline mercurous chromate, which settles out quickly ; if the precipitation is complete, the supernatant liquid will be colourless. Allow to cool, filter off the precipitate through a Whatman No. 40 or No. 540 filter paper, and wash it thoroughly with a cold 2·5 per cent aqueous solution of mercurous nitrate. Dry the filter and precipitate at 100°C. Transfer the filter and precipitate to a weighed porcelain or platinum crucible, heat gently at first and afterwards with the full Méker flame in an oxidising atmosphere until constancy of weight is attained. Weigh as Cr_2O_3. *Owing to the poisonous nature of the mercury fumes, the whole operation concerned with the ignition of the precipitate must be carried out in a fume cupboard provided with a good draught.*

Notes. 1. A suitable solution for practice may be prepared by dissolving 0·5 to 0·6 g. of A.R. potassium dichromate, accurately weighed, in 250 ml. of water.

2. Prepare the mercurous nitrate solution as follows. Moisten 3 to 4 g. of A.R. mercurious nitrate in a test tube with 2 drops of concentrated nitric acid, add 10 ml. of water, and warm until the salt dissolves. Dilute the solution somewhat before use.

C. Determination of chromium as barium chromate. *Procedure.* The solution should contain about 0·1 g. of Cr as chromate, be neutral or weakly acid with acetic acid, and occupy a volume of 200 to 300 ml. Add a 10 per cent solution of barium acetate dropwise from a burette and with constant stirring to the boiling solution (1) until present in slight excess. Place the beaker on a water bath until the precipitate settles; test for completeness of precipitation by adding a little more of the reagent. Allow to cool, filter through a weighed Gooch or porous porcelain crucible, wash with hot water until 1 ml. of the washings gives no precipitate with a little dilute sulphuric acid. Complete the determination as described in Section **IV, 45B.** Weigh as $BaCrO_4$.

Note. 1. A solution for practice may be prepared by dissolving about 0·5 g. of A.R. potassium dichromate, accurately weighed, in 300 ml. of water, adding ammonia solution until neutral, and then 1 ml. of 6*N* acetic acid.

IV, 31. Iron.

Discussion. Iron may be determined in the following forms:

A. Ferric oxide, Fe_2O_3. The precipitation of iron as ferric hydroxide by ammonia solution, etc., and its conversion into ferric oxide, in which form it is weighed, is fully described in Section **IV, 8.** Precipitation with ammonia solution yields a gelatinous precipitate which is somewhat difficult to wash and to filter; this difficulty is partly overcome by the use of macerated filter paper.

There are, however, three methods of precipitation which yield ferric hydroxide in a relatively dense and granular form, which is easily washed and filtered. These are:

(i) The potassium cyanate method. This has already been discussed under Chromium, Section **IV, 30.**

(ii) The hexamethylenetetramine method. This is based upon the slow hydrolysis of hexamethylenetetramine in acid solution:

$$2FeCl_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + 6HCl;$$

$$(CH_2)_6N_4 + 10H_2O \rightleftharpoons 6HCHO \text{ (formaldehyde)} + 4NH_4OH.$$

Separation of ferric iron is effected from manganese, zinc, cobalt and nickel, but not from aluminium, chromium and titanium, which are precipitated. If calcium is present, there is no risk of coprecipitation as carbonate, as when ammonia solution is used, for the latter reagent frequently contains traces of carbonate.

(iii) The hydrazine hydrate method. This procedure is particularly valuable in the separation of ferric iron from manganese. Precipitation must be carried out in neutral or slightly alkaline solution, for in acid solution reduction to the ferrous state occurs.

Full experimental details for each of these methods will be given.

Attention is directed to the fact that if ignition is carried out in a platinum crucible at a temperature above 1100°C some reduction to triferric tetroxide Fe_3O_4 may occur, and at temperatures above 1200°C some of the oxide may be reduced to the metal and alloy with the platinum. This accounts in part for the contamination of the platinum crucible by iron which sometimes occurs in analytical work. No magnetic oxide of iron is produced if Main-Smith crucibles (Section **II, 36B**) are employed for the ignitions.

B. Ferric cupferron and subsequent weighing as ferric oxide. Cupferron, the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N(NO){\cdot}ONH_4$, precipitates iron, vanadium, titanium and zirconium from strongly acid solutions, thus affording a separation from aluminium, chromium, beryllium, phosphorus, boron, manganese, zinc, nickel, cobalt, and sexivalent uranium. Copper and thorium must be precipitated from weakly acid solutions. Several metals (*e.g.*, lead, silver, mercury, bismuth, tungsten and cerium) interfere, but most of these may usually be removed by other methods—for example, by hydrogen sulphide in acid solution. The precipitate cannot be weighed as such, but must be ignited to the oxide. The ignition must be very carefully carried out in the early stages in order to avoid mechanical losses, for wet precipitates tend to liquefy and effervesce, whilst dry precipitates give off considerable volatile matter. The precipitate is rather bulky, and the amount of material taken should therefore be such as to yield 0·1 to 0·2 g. of ferric oxide.

A. Determination of iron as hydroxide by hydrolysis of potassium cyanate. *Procedure.* The solution (200 ml.) should contain 0·15 to 0·20 g. of Fe in the ferric state. Add a few drops of concentrated hydrochloric acid, and heat to boiling (1). Add a concentrated aqueous solution containing 2 g. of potassium cyanate to the boiling solution as rapidly as possible, with vigorous stirring (2). Boil the solution for 2 to 3 minutes, and allow the precipitate to settle. Wash well by decantation with hot water, filter off, and complete the determination as in Section **IV, 30A.** It is better to ignite the wet filter paper and precipitate in a Main-Smith crucible. Weigh as Fe_2O_3.

Notes. 1. If the yellowish solution darkens during heating, add more hydrochloric acid to bring back the solution to the original colour.

2. The cyanate solution cannot be added all at once, for frothing will then be excessive. It is important that the ferric hydroxide sol stage be passed through as quickly as possible.

A′. Determination of iron as hydroxide by means of hexamethylenetetramine. *Procedure.* The solution (200 ml.) should be faintly acid and contain about 0·1 g. of Fe in the ferric state. To the cold solution add 20 g. of ammonium chloride, followed by excess of a 10 per cent aqueous solution of hexamethylenetetramine with stirring. Allow the precipitate to settle, decant the mother liquor through a Whatman No. 41 or No. 541 filter paper, wash the precipitate by decantation with hot water, transfer to the filter (1), and again wash with hot water. Ignite the precipitate and weigh as, Fe_2O_3.

Note. 1. If a tenacious film of the precipitate adheres to the beaker, dissolve it in a few drops of concentrated hydrochloric acid, and reprecipitate with ammonia solution.

A″. Determination of iron as hydroxide by means of hydrazine hydrate. *Procedure.* The solution (100 ml.) should contain about 0·1 g. of Fe in the ferric state. Add 8 g. of ammonium chloride, a few drops of methyl red indicator, and neutralise with ammonia solution (methyl red turns yellow). Then add in one operation a slight excess of hydrazine hydrate solution (1), and boil for a short time. Filter through a Whatman No. 41 or No. 541 filter paper, wash with hot water containing 1 g. of ammonium chloride and 1 ml. of hydrazine hydrate per 100 ml., and then with hot water. Dry and ignite in the usual way. Weigh as Fe_2O_3.

Note. 1. Prepared by adding 4 ml. of hydrazine hydrate (*poisonous*) to 100 ml. of water.

B. Determination of iron with cupferron. *Procedure.* The solution (1) (150 to 200 ml.) should contain about 0·1 g. of Fe in the ferric state and be strongly acid with hydrochloric acid or sulphuric acid. To the cooled solution (*ca.* 10°C) add a freshly-prepared, filtered 5 per cent aqueous cupferron solution (2) slowly and with constant and vigorous stirring until no further formation of a brown precipitate takes place. The formation of a white precipitate of nitrosophenylhydroxylamine indicates when the reagent is present in excess. Do not warm since the reagent is rapidly decomposed in hot acid solution. Add a Whatman accelerator (or a third of a Whatman ashless tablet), stir for 2 to 3 minutes, and without further delay filter through a Whatman No. 41 or No. 541 filter paper. Wash several times with 10 per cent by volume of hydrochloric acid containing 1·5 g. of cupferron per litre, then twice with 5*N* ammonia solution to remove excess of cupferron, and finally once with water. Ignite the precipitate with the paper in a weighed porcelain, silica or platinum crucible (best in a Main-Smith crucible, Section **II, 36B**) very gently at first until all the organic matter is destroyed, and then strongly to constant weight. Weigh as Fe_2O_3.

Notes. 1. A suitable solution for practice may be prepared by weighing out accurately 0·8 to 0·9 g. of A.R. iron alum, dissolving it in 150 ml. of water, and adding 25 ml. of concentrated hydrochloric acid.

2. Only freshly-prepared solutions should be employed, because the solution only keeps for a day or two. The dry reagent should be kept in a cool dark place, and preferably with a bag of ammonium carbonate suspended in the bottle.

IV, 32. NICKEL

Discussion. Nickel may be determined in one of the following forms :

A. Nickel dimethylglyoxime, $Ni(C_4H_7O_2N_2)_2$. Full details of this estimation are given in Section **IV, 12.**

B. Nickel salicylaldoxime, $Ni(C_7H_6O_2N)_2$. The complex is precipitated in neutral or very faintly acid solutions (best at $pH = 7$) in contrast to that of copper (Section **IV, 19C**), which is formed in the presence of acetic acid. The experimental details are similar to those already given for Copper, except that the solution must be neutral or very faintly acid. Experimental details for the separation of copper and nickel with salicylaldoxime are given below.

C. $[Ni(C_5H_5N)_4](CNS)_2$; pyridine method. This is a rapid method similar in advantages and limitations to those described for copper (Section **IV, 19E**), cobalt (Section **IV, 33D**) and zinc (Section **IV, 34D**). A determination may be completed in about 30 minutes.

D. Metallic nickel. Experimental details of the electrolytic method are given in Section **IV, 81.**

B. Determination of nickel in the presence of copper with salicylaldoxime. *Procedure.* Treat the solution, free from mineral acid and containing both nickel (not more than 0·03 g.) and copper (about 0·03 g.), with 1 g. of sodium acetate and 10 ml. of glacial acetic acid per 100 ml. of solution.* Add excess of salicylaldoxime reagent over the quantity required to precipitate both metals, and stir the solution vigorously during the addition. Filter off the precipitated copper complex on a weighed filter crucible (Gooch, sintered glass, or porous porcelain), wash well with cold water, and dry at 100° to 105°C to constant weight. Weigh as $Cu(C_7H_6O_2N)_2$. Calculate the weight of copper present. Add dilute ammonia solution to the filtrate and washings (diluted to 400 to 350 mls.) until the solution is very faintly acid or alkaline. Stir thoroughly to coagulate the precipitate of nickel salicylaldoxime. Filter through a weighed sintered glass or porous porcelain crucible, wash with cold water until the washings give no colouration with ferric chloride solution, and dry at 100°C to constant weight. Weigh as $Ni(C_7H_6O_2N)_2$. Calculate the weight of nickel present.

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* The best pH range for the precipitation of copper in the presence of nickel is 2·6 to 3·1.

C. Determination of nickel by the pyridine method. *Procedure.* The solution (100 ml.) should contain about 0·1 g. of nickel (1) and be neutral in reaction. Stir in 0·5 to 1·0 g. of A.R. ammonium thiocyanate, heat to boiling, add 1 to 2 ml. of pure pyridine, and immediately remove the flame. Stir for 2 to 5 seconds until the precipitate commences to separate in sky-blue prisms. (The precipitate separates immediately or after standing a short time according to the quantity of nickel present.) When cold, filter through a weighed sintered glass or porous porcelain crucible, and use *solution 1* to assist in the transfer of the precipitate to the crucible. Wash 4 to 5 times with *solution 2,* then twice with 1 ml. portions of *solution 3,* and finally 5 or 6 times with 1 ml. portions *solution* 4. Dry in a vacuum desiccator at room temperature for 10 minutes and weigh. Repeat the drying until the weight is constant. Weigh as $[Ni(C_5H_5N)_4](CNS)_2$ (2).

Solution 1. 100 Ml. of water containing 0·4 g. of NH_4CNS and 0·6 ml. of pyridine.

Solution 2. 61·5 Ml. of water, 37·0 ml. of 95 per cent alcohol, 0·1 g. of NH_4CNS, and 1·5 ml. of pyridine.

Solution 3. 10 Ml. of absolute alcohol and 0·5 ml. of pyridine.

Solution 4. 20 Ml. of absolute (sodium dried) ether and 2 drops of pyridine.

Notes. 1. For practice in this estimation, the student may employ 0·3 g. accurately weighed, of A.R. nickel sulphate.

2. For further experimental details, see under Copper and Zinc.

IV, 33. COBALT

Discussion. Cobalt may be separated in one of the following forms :

A. Cobalti α-nitroso-β-naphtholate, $Co(C_{10}H_6O_2N)_3,2H_2O$. α-Nitroso-β-naphthol gives a red precipitate with solutions of cobalt salts. The composition is substantially that of the cobalti-compound, but small quantities of impurities (probably containing some of the cobaltous compound) are present, and this renders the results somewhat inaccurate. However, by converting the cobaltous salt into cobaltic hydroxide with hydrogen peroxide and sodium hydroxide, and then precipitating the solution of cobaltic hydroxide with the reagent, the pure cobalti-α-nitroso-β-naphtholate dihydrate is obtained, and may be weighed in this form after drying at 130°C. The reagent is unstable in aqueous solution, and must be freshly prepared as required. For the limitations of the method, see Section **I, 62F.**

B. Cobalti α-nitro-β-naphtholate, $Co(C_{10}H_6O_3N)_3$. α-Nitro-β-naphthol reacts similarly to α-nitroso-β-naphthol, but has the advantage that its aqueous solution is stable. The precipitate obtained by the hydrogen peroxide-sodium hydroxide method is homogeneous, $Co(C_{10}H_6O_3N)_3$, and may be weighed as the cobalti complex after drying at 130°C.

C. Cobalt phenylthiohydantoate complex. Phenylthiohydantoic acid precipitates cobalt in ammoniacal solution in the presence of citrate as a red-brown complex of somewhat indefinite composition. The precipitate may be ignited to the oxide " Co_3O_4 " of uncertain composition, the latter fused with potassium pyrosulphate, and the cobalt in the aqueous extract determined by any of the other methods given in this Section. For the limitations and advantages of the method, see Section **I, 62H.**

D. $[Co(C_5H_5N)_4](CNS)_2$; pyridine method. If a dilute neutral solution of a cobalt salt is treated with ammonium thiocyanate and pyridine, tetra-pyridine cobalt dithiocyanate is quantitatively precipitated. The precipitate is collected and washed *inter alia* with alcohol and ether containing a little pyridine, and then dried by simply leaving in a vacuum desiccator for 5 to 15 minutes. A complete determination of cobalt may be carried out in about 30 minutes. The precipitate may be kept unchanged for several hours in a vacuum desiccator. The method can be applied in the presence of the alkali metals, magnesium, and the alkaline earth metals, but copper, cadmium, nickel, manganese and zinc must be absent. Large quantities of ammonium salts must be absent since these exert a slight solvent action upon the precipitate. If the solution is strongly acid, it should be evaporated to dryness and the residue dissolved in water.

E. Metallic cobalt. The electrolytic method is discussed in Section **IV, 82.**

A. Determination of cobalt with α-nitroso-β-naphthol. *Procedure.* Concentrate the weakly acid solution of the cobaltous salt, containing not more than 0·03 g. of Co (1), to 10 to 20 ml., and allow to cool. Treat the cold solution with 5 to 10 drops of 100-volume hydrogen peroxide, and then add $2N$ sodium hydroxide to precipitate the cobalt as cobaltic hydroxide $Co(OH)_3$; keep the beaker covered during this process since oxygen is evolved. Add 10 to 20 ml. of glacial acetic acid, warm gently to dissolve the precipitate, dilute to 200 ml. with boiling water, and treat with 10 to 20 ml. of the freshly-prepared reagent (for preparation, see Section **I, 62F**); about 0·25 g. of α-nitroso-β-naphthol is required for every 0·01 g. of Co. Heat to gentle boiling with vigorous stirring until the precipitate coagulates or settles out. The supernatant liquid should be clear and yellow. Test whether precipitation is complete by adding a little more of the reagent to the clear solution. Filter through a weighed Gooch, sintered glass or porous porcelain crucible, transfer the precipitate to the crucible with the help of a little 33 per cent acetic acid, and wash with this hot acetic acid. Finally wash the precipitate with boiling water, and dry at 130°C to constant weight. Weigh as $Co(C_{10}H_6O_2N)_3,2H_2O$.

Note. 1. A suitable solution for practice may be prepared from *ca.* 0·1 g., accurately weighed, of A.R. cobaltous sulphate or A.R. cobalt ammonium sulphate.

B. Determination of cobalt with α-nitro-β-naphthol. *Procedure.* The method is similar to that described under **A.** Concentrate the cobalt solution, weakly acid with mineral acid and containing not more than 0·03 g. of Co, to 10 to 20 ml. Treat the cold solution with 10 drops of 100-volume hydrogen peroxide, then add 2*N* sodium hydroxide to precipitate the cobaltic hydroxide, and cover with a clock glass. Dissolve the precipitate by the addition of 10 ml. of glacial acetic acid, warm gently if necessary, and dilute to 150 to 200 ml. with hot water. Add a 50 per cent excess of the reagent (for preparation, see Section **I, 62G**) slowly and with constant stirring. Heat, with stirring, to the boiling point, allow to settle, and filter through a weighed sintered glass or porous porcelain crucible. Use a little 30 per cent acetic acid to assist in the transfer of the precipitate. Wash 3 times with 30 per cent acetic acid, followed by several times with hot water, and dry at 130°C to constant weight. Weigh as $Co(C_{10}H_6O_3N)_3$.

C. Determination of cobalt with phenylthiohydantoic acid. *Procedure.* The cobaltous solution (400 ml.) should contain not more than 0·025 g. of Co and about 7 g. of citric acid. Add concentrated ammonia solution until the solution is neutral and then a further 10 ml. Add 0·7 to 1·0 g. of phenylthiohydantoic acid, dissolved in 30 ml. of hot alcohol, with vigorous stirring. Boil and stir the solution for a few minutes to cause the precipitate to rise to the surface of the liquid. Filter the bulky precipitate through a Whatman No. 41 or No. 541 filter paper, wash well with a 0·5 per cent ammonium citrate solution, and dry at 100° to 105°C. The material thus obtained is not pure cobaltous phenylthiohydantoate, and upon ignition it gives impure Co_3O_4; nevertheless, if it is ignited in a porcelain crucible over a Méker type burner, fairly accurate results are obtained by calculating as if it were Co_2O_3. However, it is usually best to fuse the impure oxide with pure potassium pyrosulphate, dissolve the cooled melt in water, and determine the cobalt by methods **A, B, D** or **E.**

D. Determination of cobalt by the pyridine method. *Procedure.* The solution (75 to 100 ml.) should be neutral and contain about 0·1 g. of Co (1). Add 0·5 to 1·0 g. of A.R. ammonium thiocyanate, heat to boiling, treat with 1 to 2 ml. of pure pyridine, and remove the source of heat immediately. Stir for 5 seconds, and allow to cool to room temperature. The solution remains clear for a short time ; as the solution cools, red shiny crystals of the complex separate. (If the precipitate on the sides of the beaker exhibits the blue colour of the di-pyridine complex, this is washed with a little water into the solution when the blue colour immediately disappears. If stirring is continued for several minutes after the addition of the pyridine, the compound soon separates in the crystalline form.) Filter through a weighed sintered glass or porous porcelain crucible ; use *solution 1* to assist in the transfer of the precipitate to the crucible. Wash the precipitate 5 or 6 times with *solution 2,* then twice with 1 ml. portions of *solution 3,* and finally 8 to 10 times with small volumes (1 to 2 ml.) of *solution* 4 (for further experimental details, see Sections **IV, 19E** and **IV, 34D**). Dry in a vacuum desiccator at room temperature for 10 minutes, and weigh. Repeat the drying, etc., until the weight is constant. Weigh as $[Co(C_5H_5N)_4[(CNS)_2$.

Solution 1. 100 Ml. of water containing 0·5 g. of NH_4CNS and 0·7 ml. of pyridine.

Solution 2. 85·5 Ml. of water, 13·0 ml. of 95 per cent alcohol. 0·1 g. of NH_4CNS and 1·5 ml. of pyridine.

Solution 3. 25 Ml. of absolute alcohol and 2 ml. of pyridine.

Solution 4. 30 Ml. of absolute (sodium dried) ether and 4 drops of pyridine.

Note. 1. For practice in this estimation, the student may employ 0·3 g., accurately weighed or of A.R. cobalt ammonium sulphate of A.R. cobaltous sulphate.

If the solution is weakly acid, add ammonium thiocyanate, then pyridine until a precipitate appears, warm until the precipitate dissolves, add 1 to 1·5 ml. of pyridine, and immediately remove the source of heat.

IV, 34. ZINC

Discussion. Zinc may be determined in any of the following forms:

A. Zinc ammonium phosphate, $ZnNH_4PO_4$, or zinc pyrophosphate, $Zn_2P_2O_7$. The zinc is precipitated, with close adherence to the experimental conditions detailed below, as zinc ammonium phosphate $ZnNH_4PO_4,6H_2O$ and weighed either as $ZnNH_4PO_4$ (after drying at 105°C) or as $Zn_2P_2O_7$ (after ignition at 900° to 1000°C). The method is of limited application because of the numerous other elements which form sparingly soluble phosphates.

The precipitant is diammonium hydrogen phosphate $(NH_4)_2HPO_4$, which exerts an important buffering action :

$$ZnCl_2 + (NH_4)_2HPO_4 = ZnNH_4PO_4 + NH_4Cl + HCl\,;$$
$$HCl + (NH_4)_2HPO_4 = NH_4H_2PO_4 + NH_4Cl.$$

It has been shown that the most satisfactory results are obtained over the *p*H range 6·4 to 6·9 (optimum *p*H is 6·6), and that when the *p*H exceeds 7·0 the precipitate is removed from the beaker with difficulty. A solution containing 5 to 10 g. of ammonium chloride, 10 ml. of 2*N* sodium acetate and 10 ml. of 10 per cent $(NH_4)_2HPO_4$ solution in 150 ml. has a *p*H of 7·5 ; this automatically falls to 6·4 to 6·9 when heated for 2 hours on the water bath, hence this mixture is employed for precipitation.

Considerable quantities of alkali salts should be absent, for in their presence the precipitate is contaminated with zinc sodium (or potassium) phosphate. These may be removed by double precipitation ; the precipitate is dissolved in the minimum volume of dilute hydrochloric acid and reprecipitated.

B. Zinc sulphide, ZnS, and subsequent weighing either as ZnS or as $ZnNH_4PO_4$. The zinc is precipitated as zinc sulphide under carefully controlled conditions. By the use of a chloroacetic acid-sodium acetate buffer mixture, a *p*H of 2·6 to 2·7 is obtained, and the sulphide separates in a granular form. This method may be used for the separation of zinc from manganese, nickel, cobalt (concentration $\not>$ 6 per cent of zinc), iron, aluminium, chromium, and uranium. The zinc sulphide may be weighed as such after heating with excess of pure sulphur in a current of hydrogen, or it may be dissolved in 1 : 1 hydrochloric acid, the hydrogen sulphide removed, and precipitated and weighed as in **A**.

C. Zinc quinaldinate, $Zn(C_{10}H_6ON_2)_2,H_2O$. Quinaldinic acid or its sodium salt precipitates zinc quantitatively from dilute acetic acid or slightly ammoniacal solutions. Iron, aluminium, chromium, beryllium, titanium, and uranium interfere in acid solution, but in the presence of alkali tartrate in alkaline solution only zinc precipitates. The reagent is expensive, but may be recovered (see Section **I, 62N**).

D. $[Zn(C_5H_5N)_2](CSN)_2$; pyridine method. This method is a very rapid one, but unless the various wash solutions are carefully prepared, low results will be obtained. The complex may be kept unchanged in a vacuum desiccator for 2 to 3 hours (see Section **I, 62L**). Large quantities of ammonium salts must not be present as these exert a slight solvent action upon the precipitate. If the solution is strongly acid, it must be evaporated to dryness and the residue dissolved in water.

E. Metallic Zinc. For details of the electrolytic determination see Section **IV, 84.**

A. Determination of zinc as the ammonium phosphate or as the pyrophosphate. *Procedure.* To the solution containing, about 0·1 g. of Zn (1) add 5 g. of ammonium chloride, 10 ml. of 2*N* sodium acetate, and dilute to 140 ml. Heat on a water bath, and, when hot, treat with 10 ml. of 10 per cent A.R. ammonium phosphate $(NH_4)_2HPO_4$ added slowly from a pipette or burette. Heat on a water bath for 2 hours in a covered beaker, filter through a weighed crucible (Gooch, sintered glass or porous porcelain), wash with about 150 ml. of cold water, 5 ml. of 95 per cent alcohol, and dry to constant weight at 105°C (*ca.* 1 hour). Weigh as $ZnNH_4PO_4$.(2)

To weigh as the **pyrophosphate,** filter through a weighed silica Gooch, porous porcelain, or quartz filter crucible (Section **II, 33**), and ignite slowly at 900°C in an electrically heated muffle furnace to constant weight. If a muffle furnace is not available, place the crucible within a larger nickel crucible (Fig. 2-33), heat with a Méker type of burner slowly at first and then to redness until constant weight is attained. Weigh as $Zn_2P_2O_7$.

Note. 1. A suitable solution for practice may be prepared by dissolving about 0·4 g., accurately weighed, of A.R. zinc sulphate in about 75 ml. of water. A better method is to prepare pure zinc ammonium sulphate $ZnSO_4,(NH_4)_2SO_4,6H_2O$ by mixing equimolecular amounts of A.R. zinc sulphate and A.R. ammonium sulphate dissolved in boiling water, and recrystallising the product twice from hot water. The crystals are air dried, and 0·6 g., accurately weighed, is dissolved in 75 ml. of water.

2. A more rapid, but less accurate method of weighing the precipitate, collected on a sintered glass or porous porcelain crucible, is as follows (J. Dick, 1930). After washing with cold water, wash the zinc ammonium phosphate 5 or 6 times with small volumes of rectified spirit and then 5 times with small portions of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible dry with a clean linen cloth, leave in a vacuum desiccator for 10 minutes, and weigh as $ZnNH_4PO_4,H_2O$ which contains 33·28 per cent of Zn.

B. Determination of zinc as sulphide. *Procedure.* The zinc solution may contain up to 0·3 g. of Zn as chloride or nitrate, and should occupy a volume of 10 to 20 ml. (1). Treat the solution dropwise with 2*N* sodium hydroxide until there is a slight permanent turbidity. Add 10 ml. of 2*N* chloroacetic acid ($ClCH_2COOH$) with stirring and, after the solution has become clear, introduce 10 ml. of *N* sodium acetate. Transfer quantitatively to a conical flask and dilute to 150 ml. Fit the flask with a two-hole rubber stopper carrying an inlet tube extending well down into the flask and an outlet tube flush with the bottom of the stopper. Pass in hydrogen sulphide rapidly for 10 to 15 minutes, and allow to stand for 10 to 20 minutes when the white and granular precipitate of zinc sulphide will settle to the bottom of the flask. Filter on a weighed porous porcelain crucible (A_2) and wash 4 times with *solution 1* (2) if other metals are present, followed by 4 (1/2) times with *solution 2* (3). When zinc alone is present, only *solution 2* is necessary.

Weighing as ZnS. Dry the crucible at 110° to 120°C, cover the precipitate with a layer of pure sulphur (which has been recrystallised from carbon bisulphide), place a perforated Rose crucible cover on the crucible (Fig. 4-1), pass a stream of hydrogen through it (the wash bottle contains concentrated sulphuric acid), and heat the crucible at first over a small flame until the excess of sulphur has disappeared, and finally so that the bottom of the crucible glows very faintly for a few minutes. Allow the crucible to cool in hydrogen, and weigh as ZnS after leaving in a desiccator for 15 minutes.

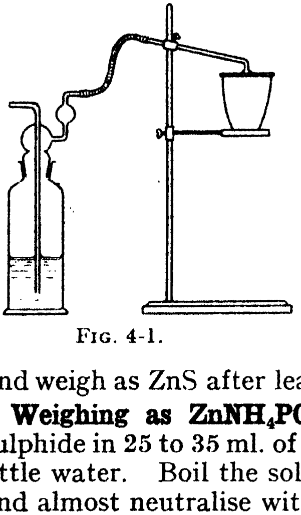

FIG. 4-1.

Weighing as $ZnNH_4PO_4$. Dissolve the precipitated zinc sulphide in 25 to 35 ml. of 1 : 1 hydrochloric acid, followed by a little water. Boil the solution to remove hydrogen sulphide, and almost neutralise with ammonia solution. Complete the estimation as in **A.** Weigh as $ZnNH_4PO_4$.

Notes. 1. If the original solution is acid, evaporate to dryness, and dissolve in 10 to 20 ml. of water.

2. *Solution* 1 : 10 ml. of 2*N* chloracetic acid and 10 ml. of *N* sodium acetate in 150 ml. water and saturated with hydrogen sulphide in the cold.

3. *Solution* 2 : four per cent acetic acid saturated with hydrogen sulphide in the cold.

C. Determination of zinc as quinaldinate. *Procedure.* The solution (150 ml.) should be neutral or weakly acid with acetic acid, and contain about 0·1 g. of Zn. Precipitate in the cold by the slow addition, with stirring, of 25 to 30 ml. of the reagent (for preparation, see Section **I, 62N**). The precipitate will settle out completely after about 20 minutes. Filter through a weighed Gooch, sintered glass or porous porcelain crucible, wash with alcohol, and dry at 105° to 110°C to constant weight. Weigh as $Zn(C_{10}H_6O_2N)_2,H_2O$.

D. Determination of zinc by the pyridine method. *Procedure.* The solution (75 ml.) should contain about 0·05 g. of zinc (1) and be neutral or very faintly acid. To the cold solution add 1 g. of solid A.R. ammonium thiocyanate, followed by 1 ml. of pure pyridine. Shake vigorously, when a white crystalline precipitate will separate. (Precipitation may also be carried out in hot solution ; the complex separates in comparatively large crystals on cooling.) Allow to stand for 15 minutes, and stir frequently. Filter through a weighed sintered glass or porous porcelain crucible, and transfer the precipitate to the crucible with the aid of *solution 1.* Wash the precipitate 4 times with *solution 2,* then wash the walls of the crucible with 1 ml. portions of *solution 3* (use a 1 or 2 ml. pipette for this process), and finally 5 to 6 times with 1 to 2 ml. volumes of *solution 4.* It is important to suck well on the pump between each washing ; it is also advantageous to stir the precipitate with a thin glass rod when washing with solutions *3* and *4.* Dry the crucible and precipitate in a vacuum desiccator (preferably of the type shown in Fig. 2-10*B*) for 15 minutes, and weigh. Repeat the drying process until the weight is constant. Weigh as $[Zn(C_5H_5N)_2](CNS)_2$.

Solution 1. 100 Ml. of water containing 0·3 g. of NH_4CNS and 0·5 ml. of pyridine.

Solution 2. 85·5 Ml. of water, 13 ml. of 95 per cent alcohol, 0·1 g. of NH_4CNS, and 1·5 ml. of pyridine.

Solution 3. 10 Ml. of absolute alcohol + 1 ml. of pyridine.

Solution 4. 15 Ml. of absolute (sodium dried) ether + 2 drops of pyridine.

If the wash solutions have been prepared, the determination should be completed within an hour.

Note. 1. For practice in this estimation, the student may employ about 0·25 g., accurately weighed, of A.R. zinc sulphate, or about 0·3 g. of pure zinc ammonium sulphate (see Note to determination **A**).

IV, 35. MANGANESE

Discussion. The only method which is at all widely used for the gravimetric estimation of manganese is the precipitation as **manganese ammonium phosphate $MnNH_4PO_4,H_2O$** in slightly ammoniacal solution containing excess of ammonium salts. The precipitate may be weighed in this form after drying at 100° to 105°C, or it may be ignited and subsequently weighed as **manganese pyrophosphate $Mn_2P_2O_7$.** The latter procedure is by far the better one. The method is, however, of limited application because of the interfering influence of numerous other elements. Volumetric methods are generally preferred (see Chapter III).

Determination of manganese as the ammonium phosphate or as the pyrophosphate. *Procedure.* The solution (200 ml.) should be slightly acid, contain not more than 0·2 g. of Mn in 200 ml., and no other cations except those of the alkali metals (1). Almost neutralise the solution with dilute ammonia solution, add 20 g. of ammonium chloride, and a considerable excess of diammonium hydrogen phosphate $(NH_4)_2HPO_4$ (say, 2 g. of the solid). If a precipitate forms at this point, dissolve it by the addition of a few drops of 1 : 3 hydrochloric acid. Heat the solution almost to boiling (90° to 95°C), and add 1 : 3 ammonia solution dropwise and with constant stirring until a precipitate ($Mn_3(PO_4)_2$) begins to form ; immediately suspend the addition of the alkali. Continue the heating and stirring until the precipitate becomes crystalline ($MnNH_4PO_4,H_2O$). Then add another drop or two of ammonia solution, stir as before, etc., and so continue until no more precipitate is produced and its silky appearance remains unchanged. The precipitate must be maintained at 90° to 95°C throughout ; a large excess of ammonia solution must be avoided. Allow the solution to stand at room temperature (or, better, at 0°C) for 2 hours. Filter through a quantitative filter paper or through a weighed porous porcelain crucible, and wash the precipitate with cold, 10 per cent ammonium nitrate solution until free from chloride. Dry at a gentle heat, ignite at as low a temperature as possible until the carbon is oxidised (2), and then heat at 1000°C (in an electric crucible furnace or within a larger nickel crucible) to constant weight. Weigh as $Mn_2P_2O_7$. Alternatively, but less desirably, the precipitate in the porous porcelain crucible may be dried at 100° to 105°C to constant weight and weighed as $MnNH_4PO_4,H_2O$ (3) ; in this case, a Gooch or sintered glass crucible may also be used.

Notes. 1. A suitable solution for practice may be prepared by one of the following methods :

(*a*) Dissolve 0·7 g., accurately weighed, of A.R. manganous sulphate $MnSO_4,4H_2O$ in 200 ml. of water.

(*b*) Dissolve 0·5 g., accurately weighed, of A.R. potassium permanganate in very dilute sulphuric acid, and reduce the solution with sulphur dioxide or with alcohol (see reduction of potassium dichromate, Section **IV, 30C**). Remove the excess of sulphur dioxide or of acetaldehyde (and alcohol) by boiling. Dilute to 200 ml.

2. These remarks apply, of course, when filter paper is used.

3. The precipitate, collected on porous porcelain or sintered glass crucible, may be weighed more rapidly but less accurately as follows (J. Dick, 1930). Wash the manganese ammonium phosphate 5 or 6 times with rectified spirit, 5 times with small volumes of anhydrous ether, and then suck the precipitate

dry at the pump for 10 minutes. Wipe the outside of the crucible dry with a clean linen cloth and leave in a vacuum desiccator for 10 minutes. Weigh as $MnNH_4PO_4.H_2O$ which contains 29.53 per cent of Mn.

IV, 36. VANADIUM

Discussion. This element, as vanadate, may be determined in one of the following forms :

A. Mercurous vanadate Hg_3VO_4 and subsequent weighing as vanadium pentoxide V_2O_5. This method is applicable only in the absence of substances which gives precipitates with mercurous nitrate solution (*e.g.*, chromate, arsenate, molybdate, tungstate and phosphate). Actually the precipitate obtained in the determination consists of a mixture of mercurous ortho- and pyro-vanadates ; this is ignited to, and weighed as, vanadium pentoxide. The solution may contain free nitric acid but not ammonium salts.

B. Silver vanadate, Ag_3VO_4. Vanadates are precipitated by excess of silver nitrate solution in the presence of sodium acetate, followed by boiling, as silver orthovanadate. The following reactions occur with a solution of a metavanadate :

$$2NaVO_3 + 2Na.C_2H_3O_2 + H_2O \rightleftharpoons Na_4V_2O_7 + 2H.C_2H_3O_2 ;$$

$$Na_4V_2O_7 + 4AgNO_3 \rightleftharpoons Ag_4V_2O_7 + 4NaNO_3 ;$$

$$Ag_4V_2O_7 + 2AgNO_3 + 2Na.C_2H_3O_2 \rightleftharpoons 2Ag_3VO_4 + 2H.C_2H_3O_2 + 2NaNO_3.$$

Volumetric methods (see Chapter III) are, however, more convenient, less influenced by interfering elements, and are generally preferred.

A. Determination of vanadium as mercurous vanadate and ignition to vanadium pentoxide. *Procedure.* The alkali vanadate solution (100 ml.) should be faintly acid with nitric acid, and contain not more than 0·1 g. of vanadium as vanadate in 100 ml. of solution. Add 5 ml. of 20-volume hydrogen peroxide and then mercurous nitrate solution (1) dropwise until, after the precipitate has settled, a further addition of 2 to 3 ml. of the reagent causes no precipitation. Boil the covered beaker for 30 minutes to destroy the excess of hydrogen peroxide, and then allow the grey precipitate to settle. Filter the precipitate through a Whatman No. 40 or No. 540 filter paper, and wash it with water containing a few drops of mercurous nitrate solution. Dry the filter and precipitate in the steam oven (or at 100°C), ash the filter paper apart from the precipitate (Section **II, 36C**) in a weighed porcelain, silica or platinum crucible, ignite gently at first and then strongly with a Méker type burner to constant weight. Alternatively, the precipitate may be collected in a weighed porous porcelain crucible ; ignition is carried out by placing the latter in a nickel crucible (Fig. 2-33) or in an electric muffle furnace. Weigh as V_2O_5. *Owing to the poisonous nature of mercury fumes, the whole of the operation concerned with the ignition must be carried out in a fume cupboard which is provided with a good draught.*

Note. 1. For preparation of mercurous nitrate solution, see Note 1 in Section **IV, 30B.**

B. Determination of vanadium as silver vanadate. *Procedure.* Neutralise the solution (200 ml.), containing not more than 0·2 g. of alkali vanadate, if acid, by aqueous sodium hydroxide, or, if alkaline, by the addition of nitric acid to the boiling solution until it becomes yellow, followed by decolourisation with dilute ammonia solution. Add 3 g. of ammonium acetate, 0·5 ml. of concentrated ammonia solution, and then excess of silver nitrate solution, heat to boiling and then keep on a steam bath for 30 minutes. Test for complete precipitation with more silver nitrate solution ; if a turbidity is produced, boil the liquid until it becomes clear. Allow the dense brown precipitate of silver vanadate to settle, and collect it on a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash with hot water, dry at 110°C, and ignite gently to constant weight within a larger crucible. Weigh as Ag_3VO_4.

IV, 37. URANIUM

Discussion. Uranium, as uranyl salts, may be determined in either of the following forms :

A. Ammonium diuranate, $(NH_4)_2U_2O_7$, and ignition to uranous uranate, U_3O_8. The uranyl solution is precipitated by ammonium hydroxide solution as ammonium diuranate ; the latter is ignited to, and weighed as, uranium oxide U_3O_8. All elements that are precipitable by ammonia solution must be absent. The reagents and solutions must be free from carbonates and organic matter, both of which prevent precipitation of the uranium.

B. Uranyl " oxinate," $UO_2(C_9H_6ON)_2,C_9H_7ON$. The formula of the compound is noteworthy, for it differs from all other metallic " oxinates " (compare Section **I, 62C**). This method may also be employed for the volumetric determination of uranium with standard potassium bromate solution (compare Section **III, 138**). Here 1 ml. N $KBrO_3 \equiv 0{\cdot}01985$ g. U.

A. Determination of uranium as ammonium diuranate. *Procedure.* The uranium should be in the form of uranyl sulphate in dilute sulphuric acid solution ; the uranyl sulphate content should not exceed 1 per cent. Add a few drops of methyl red indicator, heat to boiling, and treat with dilute ammonia solution that is free from carbonate until the indicator just becomes distinctly yellow (the precipitate also is yellow). Add a Whatman accelerator or one-third of an ashless tablet, and warm for 1 or 2 minutes. Filter off on a Whatman No. 41 or No. 541 filter paper, and wash the precipitate well with a hot 2 per cent solution of ammonium nitrate. Dry the wet paper and precipitate in a platinum or a Main-Smith crucible at as low a temperature as possible until the carbon is destroyed, and then heat strongly over a Méker (or similar) burner, the crucible being placed in a slanting position so as to maintain good oxidising conditions (with the Main-Smith crucible, the lid should be removed and placed on one side). Cool in a desiccator and weigh. Repeat the ignition until constant weight is attained. Weigh as U_3O_8.

B. Determination of uranium with oxine. *Procedure.* The uranium should be in the form of uranyl nitrate or chloride in 1 to 2 per cent acetic acid solution (1), and the solution may contain up to 0·3 g. of U. Add 5 g. of ammonium acetate, heat to boiling, and add slowly a four-fold excess of the oxine reagent (2). Digest on the water bath for a short time, and allow to cool. When cold, filter on a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash thoroughly with hot water until the excess of oxine has been removed (ferric chloride test), and then several times with cold water. Dry at 105° to 110°C to constant weight. Weigh as $UO_2(C_9H_6ON)_2,C_9H_7ON$.

Notes. 1. If the solution contains mineral acid, almost neutralise with ammonia solution, add 5 g. of ammonium acetate and then sufficient acetic acid to give a 1 to 2 per cent acid solution.

2. The oxine reagent is prepared as follows. Dissolve 3 g. of oxine in the minimum volume of glacial acetic acid, dilute to 100 ml. with water, add dilute ammonia solution dropwise until a permanent slight precipitate separates, and just dissolve the latter by the addition of a little dilute acetic acid. Alternatively, the method of Section **I, 62P** may be used.

IV, 38. THORIUM

Discussion. Thorium may be determined in either of the following forms:

A. Thorium oxalate, $Th(C_2O_4)_2$, and subsequent ignition to thoria, ThO_2. This method is of rather limited application since phosphates and all the rare earths must be absent. Thorium oxalate is soluble in ammonium oxalate solution and in strong mineral acids (concentration greater than, for example, 0·4*N* hydrochloric acid).

B. Thorium sebacate, $Th(C_4H_8CO_2)_2$, and subsequent ignition to thoria, ThO_2. This procedure permits of the separation by a single precipitation of thorium from relatively large amounts of the rare earths (Ce, La, Pr, Nd, Sa, Gd) and also from quadrivalent cerium.

A. Determination of thorium as oxalate. *Procedure.* The thorium should be in hydrochloric acid solution (100 ml.) containing not more than 3·5 per cent of hydrochloric acid by volume and not more than 0·1 g. of Th. Heat the solution (100 ml.) to boiling, and add slowly and with constant stirring sufficient of a boiling 10 per cent solution of oxalic acid to combine with all the thorium and leave an excess of 20 ml. Allow the solution to cool and stand overnight. Filter through a quantitative filter paper, wash with a solution containing 3·5 ml. of concentrated hydrochloric acid and 2·5 g. of oxalic acid per 100 ml., and ignite with the full heat of a Méker (or similar) burner (*ca.* 1100°C) in a weighed platinum, porcelain or silica crucible to constant weight. Weigh as ThO_2.

B. Determination of thorium as sebacate. *Procedure.* The solution (100 ml.) should be neutral or faintly acid, and contain not more than 0·1 g. of Th. Heat the solution to boiling and add slowly and with constant stirring a hot almost saturated solution of pure sebacic acid in slight excess. The precipitate is voluminous, but granular, and therefore easily manipulated. Filter off immediately, wash thoroughly with hot water, dry, ignite, and weigh as ThO_2 (see **A**).

IV, 39. CERIUM

Discussion. Cerium may be determined as **ceric iodate, $Ce(IO_3)_4$**, which is ignited to, and weighed as, **ceric oxide, CeO_2.** Thorium (and zirconium) must, however, be first removed (see Section **IV, 38**); the method is then applicable in the presence of relatively large quantities of rare earths. Volumetric methods (see Section **III, 82**) are generally preferred.

Determination of cerium as ceric iodate and subsequent ignition to ceria. *Procedure.* The solution should not exceed 50 ml. in volume, all metallic elements should be present as nitrates, and the cerium content should not exceed 0·11 g. Treat the solution with half its volume of concentrated nitric acid, and add 0·5 g. of potassium bromate (to oxidise the cerium). When the latter has dissolved, add 10 to 15 times the theoretical quantity of potassium iodate in nitric acid solution (1) slowly and with constant stirring, and allow the precipitated ceric iodate to settle. When cold, filter the precipitate through a fine filter paper (*e.g.*, Whatman No. 42 or No. 542), allow to drain, rinse once and then wash back into the beaker in which precipitation took place by means of a solution containing 0·8 g. of potassium iodate and 5 ml. of concentrated nitric acid in 100 ml. Mix thoroughly, collect the precipitate on the same paper, drain, wash back into the beaker with hot water, boil, and treat at once with concentrated nitric acid dropwise until the precipitate just dissolves (20 to 25 ml. of acid are required per 0·1 g. of ceria). Add 0·25 g. of potassium bromate and as much potassium iodate-nitric acid solution as before. When cold, collect the ceric iodate upon the same filter paper, wash once with the washing solution, return to the beaker, stir with the washing solution, filter again, and wash thrice with the same solution. Place the filter paper and precipitate in the same beaker, add 5 to 8 g. of oxalic acid and 50 ml. of water, and heat to boiling. After all the iodine has been expelled, set aside for several hours, filter, wash with cold water, dry and ignite to constant weight in a platinum crucible. Weigh as CeO_2.

Note. 1. This is prepared by dissolving 50 g. of potassium iodate in 167 ml. of concentrated nitric acid, and diluting to 500 ml.

IV, 40. TITANIUM

Discussion. Titanium may be determined in one of the following forms :

A. Titanium "oxinate," $TiO(C_9H_6ON)_2$. Full experimental details of this method are given in Section **III, 138**, *Procedure F*. Alkaline earth metals, magnesium and the alkali metals do not interfere. The precipitate of $TiO(C_9H_6ON)_2,2H_2O$ is collected in a weighed sintered glass or porous porcelain crucible, dried to constant weight at 110°C, and weighed as $TiO(C_9H_6ON)_2$.

B. Titanium dioxide, TiO_2, after precipitation with tannin and antipyrine. This method affords a separation from iron, aluminium, chromium, manganese, nickel, cobalt and zinc, and is applicable in the presence of phosphates and silicates. Small quantities of titanium (2 to 50 mg.) may be readily estimated.

2. Titanium dioxide, TiO_2, after precipitation with selenious acid. This procedure may be applied in the presence of aluminium, beryllium, manganese, nickel, cobalt, the alkaline earth metals and magnesium ; zinc is not precipitated, but may be occluded if the selenious acid is added too rapidly.

D. Titanium dioxide, TiO_2, after precipitation with para-hydroxyphenylarsonic acid. This procedure will separate titanium from most other commonly occurring ions by a single precipitation, Zirconium, tin, ceric cerium and hydrogen peroxide must be absent.

B. Determination of titanium with tannin and antipyrine. *Procedure.* The Ti content of the solution should not exceed 0·1 g. of TiO_2, and the titanium should be present as the sulphate or chloride. Add dilute ammonia to the solution until the odour persists, then (cautiously) 10 ml. of concentrated sulphuric acid, and 40 ml. of 10 per cent tannin solution. Dilute to 400 ml., stir thoroughly, and cool. Introduce a 20 per cent aqueous solution of antipyrine (" phenazone ") with constant stirring until an orange-red flocculent precipitate is obtained. Stop the stirring, and continue the addition of the antipyrine solution until a white cheese-like precipitate (produced by the interaction of tannin and antipyrine) is formed in addition to the red precipitate. Boil the mixture, remove the flame, add 40 g. of ammonium sulphate, and allow to cool with occasional stirring. Filter the bulky precipitate through a Whatman No. 41 or No. 541 filter paper, supported on a Whatman filter cone (hardened, No. 51), with slight suction, and wash with a solution composed of 100 ml. of water, 3 ml. of concentrated sulphuric acid, 10 g. of ammonium sulphate and 1 g. of antipyrine. Dry the precipitate at 100°C, transfer to a weighed crucible, heat gently at first and then ignite to constant weight. Weigh as TiO_2.

Note. If the wet precipitate is heated directly, caking occurs which renders the complete oxidation of the carbonaceous matter very slow. If alkali metals were originally present, the ignited titania must be washed with hot water, filtered, and re-ignited to constant weight.

C. Determination of titanium with selenious acid. *Procedure.* The titanium should be in solution in dilute acid, preferably hydrochloric acid in which precipitations and separations are more facile than in dilute sulphuric acid; the solution should contain not more than about 0·1 g. of Ti. Treat the cold acid solution of titanium with dilute ammonia solution until the acid concentration is reduced below 0·2*N*, and then add with constant stirring 5 per cent aqueous selenious acid solution until the precipitate coagulates. The precipitate has the composition $H_2[TiO_2,SeO_3],2H_2O$ and becomes anhydrous at 110°C; it adsorbs traces of selenious acid, however, so that weighing in this form is not permissible. Add a Whatman accelerator (or one-third of an ashless tablet) and allow the precipitate to settle for a few hours. Filter the precipitate through a Whatman No. 41 or No. 541 filter paper, supported upon a Whatman filter cone (hardened, No.

51), with slight suction, and wash with cold water. Transfer the wet precipitate to a weighed porcelain, silica or Main-Smith crucible, dry over a small flame, heat until all the selenium is expelled, and ignite to constant weight. Weigh as TiO_2.

D. Determination of titanium with para-hydroxy-phenylarsonic acid. *Procedure.* Dissolve the sample (1) containing not more than about 0·06 g. of TiO_2 in sulphuric or hydrochloric acid, and dilute to 200 ml. The amount of the acid present should be such that the solution will be approximately but not more than 0·60*N* in hydrochloric acid or 1·80*N* in sulphuric acid after the reagents have been added and the precipitation is complete. Heat the solution to boiling ; if iron is present, add 2 to 3 g. of A.R. ammonium thiocyanate : add 100 ml. of a 4 per cent aqueous solution of para-hydroxyphenylarsonic acid (2). Boil gently for 15 minutes to coagulate the precipitate. Allow to cool to room temperature, and filter with suction on a Whatman No. 542 or No. 42 filter paper supported on a filter cone (Whatman, No. 51, hardened). Wash the precipitate 5 or 6 times with a wash liquid of 0·25*N* hydrochloric or sulphuric acid containing about 0·5 g. of the solid reagent per 100 ml. (if iron is present, 1 to 2 g. of ammonium thiocyanate should also be added to each 100 ml. of wash liquor. Finally wash the precipitate 2 or 3 times with 2 per cent aqueous ammonium nitrate solution. Transfer the filter to a Main-Smith crucible, ignite gently at first until all the carbon is burnt off (*this operation must be carried out in a fume chamber provided with an efficient draught*) and then with the full blast of a Fisher burner until constant weight is attained. Weigh as TiO_2.

Notes. 1. For practice in this determination the U.S. Bureau of Standard " Iron Ore, No. 29 " may be used (see Section **A, 8**). Dissolve 4 g. of this in 100 ml. of dilute hydrochloric acid, and filter. Fuse the undissolved residue with sodium carbonate, wash the melt into the main filtrate, remove the silica in the usual manner, add 4 g. of A.R. ammonium thiocyanate, dilute to 200 to 250 ml., and continue the estimation as above.

2. A.R. para-hydroxy-phenylarsonic acid is supplied by the Mallinckrodt Chemical Works, New York, U.S.A. ; see Section **A, 9**.

IV, 41. ZIRCONIUM

Discussion. Zirconium may be determined in one of the following forms :

A. Secondary zirconium phosphate, $ZrH_2(PO_4)_2$, and subsequent ignition to the pyrophosphate, $Zr_2P_2O_7$. Zirconium is quantitatively precipitated from solutions containing as much as 10 per cent by volume of sulphuric acid by excess of diammonium hydrogen phosphate provided that the solution is allowed to stand at 40° to 50°C for a few hours. The precipitate is washed with a moderate amount of 5 per cent ammonium nitrate solution to remove excess of phosphate; prolonged washing results in hydrolysis of the zirconium phosphate and consequent loss of phosphate, thus introducing errors which may be as high as 1 or 2 per cent. If titanium is present, excess of hydrogen peroxide must be added before the addition of the phosphate precipitant. Cerium should preferably be in the tervalent condition; a double precipitation is required in the presence of thorium.

B. Basic zirconium selenite and subsequent ignition to the dioxide, ZrO_2. The zirconium is precipitated as the basic selenite with selenious acid in hot dilute hydrochloric acid solution, the precipitate washed with dilute hydrochloric acid, and then ignited to, and weighed as, ZrO_2. No other acids should be present, and the hydrochloric acid content should be 5 per cent and not over 7 per cent by volume. This method enables a separation to be effected by a single precipitation from the rare earths (cerium being in the tervalent condition) and from aluminium. Iron, if present up to 10 per cent of the weight of the zirconium, does not interfere if precipitation is made in dilute solution (100 to 200 ml. of solution containing 0·05 g. ZrO_2) and double the quantity of selenious acid solution is used for precipitation.

C. Zirconium *n*-propylarsonate and subsequent ignition to the dioxide, ZrO_2. Zirconium is quantitatively precipitated in dilute sulphuric acid solution by aqueous *n*-propylarsonic acid; tin interferes, but may be removed from the zirconium oxide residue obtained upon ignition by adding powdered ammonium iodide, and re-igniting (see Section **IV, 22A**). Titanium, aluminium, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum and tungsten do not interfere. Complete precipitation of the zirconium takes place in the presence of large quantities of iron, but a small quantity of iron is adsorbed upon the zirconium precipitate; the iron is completely removed by reprecipitation. The method is therefore of particular value for the analysis of complex steels containing zirconium. Full particulars are given in Section **IV, 92L**; the method for the determination of zirconium in a simple compound or mixture should be obvious from these details.

D. Zirconium para-hydroxy-phenylarsonate and subsequent ignition to the dioxide. The procedure is similar to that already given for titanium (Section **IV, 40D**) except that a mineral acid concentration of 2·5 to 3·0*N* is employed, and somewhat less reagent is necessary. Phosphates must, of course, be absent. The method is particularly applicable to the determination of zirconium in the presence of a large amount of iron.

A. Determination of zirconium as pyrophosphate. *Procedure.* The zirconium solution (100 ml.) should contain about 10 per cent by volume of concentrated sulphuric acid and about 0·05 g. of Zr. Add a few ml. of 100-volume hydrogen peroxide (" perhydrol ") to oxidise any titanium present and keep it in solution ; if titanium is known to be absent, the addition of hydrogen peroxide is unnecessary. Add a freshly prepared 10 per cent aqueous $(NH_4)_2HPO_4$ solution in 10 to 20 fold excess over that required to form $ZrH_2(PO_4)_2$. Adjust the acidity to 10 per cent by volume of sulphuric acid and digest at 40° to 50°C for a few hours ; it is advisable to add a Whatman accelerator to assist in the subsequent filtration. Allow the precipitate to settle (if only a little Zr is present, it is best to leave it overnight), filter through a quantitative filter paper, and wash with cold 5 per cent ammonium nitrate solution until free from phosphate (not more than 200 ml. should be used). Transfer the wet paper and precipitate to a weighed porcelain, platinum or, best, Main-Smith crucible, heat very gently until all the paper is charred, ignite very carefully until all the carbon has been oxidised, and then ignite to constant weight. Weigh as $Zr_2P_2O_7$.

B. Determination of zirconium with selenious acid. *Procedure.* The solution (200 ml.) should contain about 5 per cent by volume of hydrochloric acid (sulphuric acid is undesirable) and not more than 0·2 g. of zirconia. Treat with 20 ml. of 12·5 per cent aqueous selenious acid solution, and boil for a few minutes. Allow the precipitate of basic selenite to settle, filter through a quantitative filter paper, wash with hot 3 per cent hydrochloric acid containing a little selenious acid, dry in a weighed porcelain, platinum or Main-Smith crucible, and ignite to constant weight. Weigh as ZrO_2.

IV, 42. THALLIUM

Discussion. Thallium may be determined in either of the following forms :

A. Thallous chromate, Tl_2CrO_4. The thallium must be present in the thallous state. If present as a thallic salt, reduction must be effected with sulphur dioxide before precipitation ; the excess of sulphur dioxide is boiled off.

B. Thallous cobaltinitrite, $Tl_3[Co(NO_2)]$. It is possible to precipitate a thallous salt quantitatively by means of a special sodium cobaltinitrite reagent at 30° to 40°C in the presence of 5 per cent of formic acid.

A. Determination of thallium as chromate. *Procedure.* The solution (100 ml.) should contain about 0·1 g. of Tl, no excessive amounts of ammonium salts, and no substances that form precipitates with ammonia solution, or reduce potassium chromate, or react with potassium or thallous chromate in ammoniacal solution. Neutralise the thallium solution (100 ml.) with ammonia solution, and add 3 ml. in excess. Heat to about 80°C, and add 2 g. of potassium chromate in the form of a 10 per cent solution slowly and with constant stirring. Allow to stand at the laboratory temperature for at least 12 hours. Filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash with 1 per cent potassium chromate solution, then with 50 per cent alcohol, and dry at 120°C to constant weight. Weigh as Tl_2CrO_4.

B. Determination of thallium as cobaltinitrite. *Procedure.* The solution (100 ml.) should contain about 5 per cent of free formic acid, and about 0·1 to 0·2 g. of Tl ; potassium and other elements which give precipitates with the sodium cobaltinitrite reagent should be absent. Warm the solution to 30° to 40°C and add an excess of the reagent (1) at the same temperature. Allow to stand for 1 hour, collect the scarlet precipitate on a weighed sintered glass or porous porcelain crucible, wash with cold water, and dry at 100°C to constant weight. Weigh as $Tl_3[Co(NO_2)_6]$.

Note. 1. The reagent is prepared by mixing equal volumes of (*a*) 28·6 g. of cobalt nitrite and 50 ml. of 50 per cent formic acid in 500 ml. of water, and (*b*) 180 g. of sodium nitrite per 500 ml.

IV, 43. CALCIUM

Discussion. Calcium may be determined in one of the following forms : **calcium oxalate CaC_2O_4,H_2O, calcium carbonate $CaCO_3$, and calcium oxide CaO.** These methods are fully discussed in Section **IV, 10.** A clean separation from magnesium with a single precipitation may be obtained by precipitation as **calcium molybdate $CaMoO_4$** (see Section **IV, 94H** and Section **IV, 18A**).

IV, 44. STRONTIUM

Discussion. Strontium may be estimated in one of the following forms :

A. Strontium sulphate, $SrSO_4$. In this determination, the most accurate for strontium, calcium, barium and lead must be absent, and the solution (preferably hydrochloric) should be as neutral as possible. If considerable acid is present, this must be removed by evaporation. Strontium sulphate dissolves appreciably in an acid medium because of the reaction :

$$SrSO_4 + H^+ \rightleftharpoons HSO_4^- + Sr^{++}.$$

Strontium sulphate has a solubility of about 0·14 g. per litre at the ordinary temperature ; the solubility is decreased by the addition of a *slight* excess of sulphuric acid, and of alcohol.

B. Strontium oxide, SrO. The strontium is precipitated as the oxalate SrC_2O_4,H_2O, and is ignited to, and weighed as, the oxide SrO. The experimental details are similar to those given in Section **IV, 10** except that some alcohol should be added to reduce the solubility. Calcium, barium, magnesium and other interfering elements must be absent.

A. Determination of strontium as sulphate. *Procedure.* The solution (100 ml.) should contain about 0·2 g. of Sr and be slightly acid with hydrochloric acid (1). Add slowly a ten-fold excess of dilute sulphuric acid, followed by a volume of alcohol equal to that of the solution. Stir well, and allow to stand for at least 12 hours. Transfer the precipitate to a weighed silica Gooch or porous porcelain crucible, wash with 75 per cent alcohol to which a few drops of sulphuric acid have been added, and finally with pure alcohol (or rectified spirit) until the washings are free from sulphate. Dry and ignite (in a larger nickel crucible) at dull redness to constant weight. Alternatively, a filter paper may be used : here the paper should be burnt apart from the precipitate (Section **II, 36C**) (to prevent possible reduction to the sulphide), and the residue then ignited together with the main precipitate in a weighed porcelain, silica or platinum crucible. Weigh as $SrSO_4$.

Note. 1. A solution for practice in this determination may be prepared by dissolving 0·3 to 0·4 g., accurately weighed, of pure strontium carbonate (the A.R. product may be obtained from the Mallinckrodt Chemical Works, U.S.A. ; see Section **A, 9**) in a little dilute hydrochloric acid (see Section **IV, 10**), and diluting to 100 ml.

IV, 45. BARIUM

Discussion. Barium may be determined in one of the following forms :

A. Barium sulphate, $BaSO_4$. This method is most widely employed. The effect of various interfering elements and radicals (*e.g.*, calcium, strontium, lead, nitrate, etc., which contaminate the precipitate) has been fully dealt with in Section **IV, 6.**

B. Barium chromate, $BaCrO_4$. This method is of limited application because of the influence of numerous interfering elements. It is useful, however, in the separation of barium from both calcium and strontium. Barium chromate may be heated to a red heat without decomposition. If green spots of chromic oxide, due to the reduction of the chromate, should appear, continued ignition with free access of air will result in re-conversion into chromate.

A. Determination of barium as sulphate. *Procedure.* The barium solution (100 ml.) should contain not more than 0·15 g. of barium (1), and not more than 1 per cent by volume of concentrated hydrochloric acid. Heat to boiling, add a slight excess of hot *N* sulphuric acid slowly and with constant stirring. Digest on the steam bath until the precipitate has settled, filter, wash with hot water containing a few drops of sulphuric acid, and then with a little water until the acid is removed. Full experimental details of the filtration, washing and ignition processes are given in Section **IV, 6.** Weigh as $BaSO_4$.

Note. 1. A suitable solution for practice may be prepared by dissolving about 0·3 g., accurately weighed, of A.R. barium chloride in 100 ml. of water and adding 1 ml. of concentrated hydrochloric acid.

B. Determination of barium as chromate. *Procedure* 1. The solution (200 ml.) (1) should contain not more than 0·4 g. of Ba, and be neutral in reaction. Add about 1 ml. of 6*N* acetic acid to the neutral solution (200 ml.), heat to boiling, and treat with a slight excess of a hot dilute solution of ammonium chromate (2) dropwise from a burette and with constant stirring. Place the beaker on a water bath until the precipitate settles ; test for completeness of precipitation by adding a little more of the reagent. Allow to cool, filter through a weighed Gooch or porous porcelain crucible, wash with hot water until 1 ml. of the washings gives scarcely any reddish-brown colouration with neutral silver nitrate solution. Place the crucible inside a larger porcelain or nickel crucible, and heat to a temperature not exceeding dull-red heat until the precipitate has a uniform bright yellow colour, and is constant in weight. Weigh as $BaCrO_4$.

Notes. 1. A suitable solution for practice in this determination may be prepared by dissolving about 0·4 g., accurately weighed, of A.R. barium chloride in 200 ml. of water.

2. The ammonium chromate solution is prepared by dissolving 10 g. of pure ammonium chromate (free from sulphate) in 100 ml. of water, and adding dilute ammonia solution until the colour of the solution is clear yellow.

Procedure 2. The solution (100 ml.) should contain not more than 0·30 g. of Ba, and be neutral in reaction. Add 10 ml. of *N* acetic acid and 5 g. of pure ammonium chloride, and stir until the solid has dissolved. Heat to boiling, and add 10 ml. of 10 per cent A.R. potassium chromate solution slowly and with constant stirring. Boil gently for 2 to 3 minutes, and allow to stand overnight. Collect the barium chromate on a weighed filter crucible (Gooch, porous porcelain or sintered glass), wash with 50 ml. of cold water, and dry to constant weight at 130°C. Weigh as $BaCrO_4$.

IV, 46. MAGNESIUM

Discussion. Magnesium may be estimated in one of the following forms : **A. Magnesium pyrophosphate, $Mg_2P_2O_7$.** This determination is dealt with fully in Section **IV, 11.**

B. Magnesium " oxinate " (8-hydroxyquinolate), $Mg(C_9H_6ON)_2$, $2H_2O$. The experimental details, applicable if only alkali metals are present with the magnesium, have been described in Section **III, 138**, *Procedure B.*

For practice in this determination, the student may employ about 0·2 g., accurately weighed, of A.R. magnesium sulphate dissolved in 150 ml. of water. The precipitated magnesium "oxinate" is collected on a weighed sintered glass or porous porcelain crucible, well washed with warm 1% ammonia solution, dried at 100° to 105°C, and weighed as $Mg(C_9H_6ON)_2,2H_2O$. Alternatively, the precipitate may be dried at 130° to 140°C, and weighed as the anhydrous compound $Mg(C_9H_6ON)_2$.

Heavy metals, other than copper, cadmium and zinc, are prevented from interfering if the magnesium is precipitated from a solution (originally neutral) to which 10 to 20 ml. of 2*N* sodium hydroxide and 5 g. of sodium tartrate have been added. If copper, cadmium and/or zinc are present they may be precipitated from acetic acid solution by oxine, and after their separation, magnesium is determined in the filtrate by the usual method. If aluminium is present, it is precipitated in neutral or weakly acid solution by oxine (see Section **III, 138,** *Procedure A*) and the magnesium determined in the filtrate.

In all cases where metals other than those of the alkalis occur in solution, reprecipitation is necessary. The first precipitate of magnesium oxinate is dissolved in the minimum volume of dilute hydrochloric acid, 1 to 2 g. of ammonium acetate and a few drops of the oxine solution added, and the solution made just alkaline with dilute ammonia solution. The mixture is boiled for a few minutes to render the precipitate crystalline, and is then collected and weighed.

IV, 47. SODIUM

Discussion. Sodium may be determined in one of the following forms :

A. Sodium sulphate, Na_2SO_4. Any sodium compound of a volatile acid may be converted into sodium sulphate by repeated evaporation with sulphuric acid. Some bisulphate $NaHSO_4$ is formed in the process, and this is converted (via the pyrosulphate $Na_2S_2O_7$) into the normal salt with some difficulty. The latter change is facilitated by the addition of a little powdered ammonium carbonate ; this is because ammonium sulphate, which is completely volatilised on heating, is formed :

$$Na_2S_2O_7 + (NH_4)_2CO_3 = Na_2SO_4 + (NH_4)_2SO_4 + CO_2.$$

B. Sodium zinc uranyl acetate, $NaZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$. Treatment of a concentrated solution of a sodium salt with a large excess of zinc uranyl acetate reagent results in the precipitation of sodium zinc uranyl acetate. This substance is moderately soluble in water (58·5 g. per litre at 21°C) so that a special procedure must be adopted in the washing and collecting of the precipitate. Potassium does not interfere provided not more than 0·05 g. is present per ml. of solution immediately prior to the precipitation. Ammonium, calcium, strontium, barium, magnesium, iron, aluminium, and chromium do not interfere if present in reasonable amounts, but lithium, which also forms a sparingly soluble triple acetate, must be absent. Oxalates, tartrates, phosphates and arsenates, which yield precipitates with the uranyl ion, should not be present. Sulphate must be absent when potassium is present, for potassium sulphate is sparingly soluble in the reagent ; sulphate may be converted into chloride by treatment with barium chloride.

C. Sodium magnesium uranyl acetate, $NaMg(UO_2)_3(C_2H_3O_2)_9$, $6{\cdot}5H_2O$. This determination is similar to **B** except that magnesium uranyl acetate reagent is used. The method is applicable to solutions containing up to 25 mg. of Na, although with care 50 mg. may be estimated ; the volume of the solution should be 5 ml. Ammonium and calcium ions are practically without effect ; the maximum quantities of potassium permissible with 50 ml. and 100 ml. of the reagent are 0·1 g. and 0·25 g. respectively. The procedure may be applied to the determination of sodium in felspar (see Section **IV, 95F**).

A. Determination of sodium as sulphate. *Procedure.* This estimation is most conveniently carried out in a Main-Smith crucible (Section **II, 36B**). Evaporate the solution (1) to dryness in a weighed Main-Smith crucible on the water bath. Transfer to a triangle (or to hot plate, the temperature of which can be controlled), add a few ml. of concentrated sulphuric acid dropwise on to the cover of the crucible, and evaporate gently to dryness *in the fume cupboard* until fuming ceases. Repeat this operation twice. Allow to cool, add a few small pieces (about the size of a pea) of solid ammonium carbonate to decompose any pyrosulphate present, and heat to dull redness for 15 minutes. Allow to cool in a desiccator for 25 minutes, and weigh immediately at the end of this period. Repeat the ignition until constant weight is attained. Weigh as Na_2SO_4.

Note. 1. A suitable solution for practice may be prepared by weighing out accurately about 0·5 g. of A.R. sodium chloride, and dissolving it in a little water.

B. Determination of sodium as sodium zinc uranyl acetate. *Procedure.* The final solution may contain up to 0·05 g. of

Na per ml., but the method is best applied to solutions containing not more than 0·008 g. of Na per ml. Treat the concentrated sodium solution (say, 1·5 ml.) (1) with 15 ml. of zinc uranyl acetate reagent (2), and stir vigorously. Allow to stand for 1 hour, and filter through a weighed sintered glass crucible (*G*4). Wash the precipitate 4 times with 2 ml. portions of the precipitating reagent (allow the wash liquid to drain completely before adding the next portion), then 5 times with 95 per cent alcohol saturated with sodium zinc uranyl acetate (2 ml. portions), and finally with a little dry ether or acetone. Dry for 30 minutes only at 105°C. Weigh as $NaZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$.

Notes. 1. A suitable solution for practice may be prepared by evaporating 20 ml. of 0·1*N* sodium chloride, prepared from the A.R. salt, to 1·5 ml. on a water bath.

2. The reagent is prepared by mixing equal volumes of solutions *A* and *B* and filtering.

Solution A : dissolve 20 g. of crystallised uranyl acetate $UO_2(C_2H_3O_2)_2,2H_2O$ in 4 ml. of glacial acetic acid and 100 ml. of water (warming may be necessary).

Solution B : dissolve 60 g. of crystallised zinc acetate $Zn(C_2H_3O_2)_2\,3H_2O$ in 2 ml. of glacial acetic acid and 100 ml. of water.

C. Determination of sodium as sodium magnesium uranyl acetate. *Procedure.* The solution of the sodium salt should be evaporated to 5 ml. if 10 mg. or more of Na are present ; if 1 mg. is present, the volume should be reduced to 1 to 2 ml. Treat the solution (1) with excess of the clear reagent (2)—as a rough guide the number of ml. of the reagent should be 10 times the number of mg. of Na present ; excess of the reagent does no harm. Immerse the vessel in a bath maintained at 20° ± 1°C, and stir *vigorously* (preferably by means of a mechanical stirrer) for 30 to 45 minutes. Filter the precipitate immediately through a weighed sintered glass crucible, using gentle suction, and after all the solution has run through, wash the precipitate 4 to 5 times with successive 5 ml. portions of 95 per cent alcohol saturated with sodium magnesium uranyl acetate. Dry for 30 minutes at 105°C, and weigh as $NaMg(UO_2)_3(C_2H_3O_2)_9,6{\cdot}5H_2O$.

Notes. 1. A suitable solution for practice in the determination may contain 25 mg. of Na in 5 ml.

2. The reagent is prepared as follows :

Solution A : 21·3 g. of crystallised uranyl acetate, 15 g. of glacial acetic acid and 250 ml. of water.

Solution B : 125 g. of crystallised magnesium acetate $Mg(C_2H_3O_2)_2,6H_2O$, 15 g. of glacial acetic acid, and 250 ml. of water.

Heat solutions *A* and *B* separately to 70°C until all the salts are dissolved, and then mix the solutions at 70°C, and allow to cool to 20°C. Place the vessel containing the mixed reagent in water at 20° ± 1°C, and maintain at this temperature for 1 to 2 hours until the slight excess of salts has crystallised out. Filter through a dry filter into a dry bottle. The solution is stable for prolonged periods (8 months) if kept away from direct sunlight.

IV, 48. POTASSIUM

Discussion. Potassium may be determined in one of the following forms:

A. Potassium chloroplatinate, $K_2[PtCl_6]$. This method is applicable only to those potassium compounds which can be completely converted into potassium chloride by evaporation with hydrochloric acid (as by technique of Section **IV, 47A**), because it is only from a solution containing chloride that potassium can be completely precipitated as $K_2[PtCl_6]$ by chloroplatinic acid solution. Ammonium salts and all metals other than sodium and potassium must be removed, as must also sulphate, phosphate and similar radicals. Sodium chloroplatinate is soluble in 80 per cent alcohol, hence this method provides a means of separation of sodium from potassium. Indeed, potassium was frequently determined by this method when a separation from sodium was required. In recent years this separation has been superseded by the procedure employing the less expensive perchloric acid (see **B** below).

The potassium chloroplatinate may be reduced by magnesium to the metal and weighed as such. If this method is adopted, potassium may be estimated in the presence of phosphates, sulphates, calcium, magnesium and many other metals.

B. Potassium perchlorate, $KClO_4$. This method employs the comparatively inexpensive perchloric acid as the precipitating reagent. All metals and ammonium, other than those of the alkali metals, should be absent; the metals should be in the form of chlorides. Under these conditions the procedure may be employed for the **quantitative separation of potassium, sodium and lithium.** The three metals, as chlorides, are converted into the perchlorates by evaporation with perchloric acid (**DANGER,** see Section **IV, 70**). The mixed perchlorates are treated with a mixture of equal volumes of anhydrous *n*-butyl alcohol (b.p. 116° to 118°C/760 mm.) and absolute ethyl acetate. This dissolves the sodium and lithium perchlorates leaving the potassium perchlorate, which can be weighed. The ethyl acetate in the washings is removed by evaporation, and the sodium is precipitated as sodium chloride by the addition of a solution of hydrogen chloride in *n*-butyl alcohol. This is filtered off and weighed. The filtrate from the sodium is evaporated, and the lithium is determined as sulphate.

If potassium alone is to be determined, many other metals may be present as nitrates or chlorides; these include those of the alkaline earth metals and magnesium, but ammonium salts and sulphates must be absent. In this instance it is sufficient to use 98 per cent alcohol saturated with potassium perchlorate and containing a little perchloric acid to remove the perchlorates of the metals other than sodium. This method is also fairly accurate when applied to a mixture of sodium and potassium chlorides.

C. Potassium sulphate, K_2SO_4. The experimental details are similar to those given in Section **IV, 47A.** The method is applicable to any potassium compound of any volatile acid. All other metals must be absent. The temperature of ignition must not exceed 800°C owing to the danger of loss by volatilisation above this temperature.

D. Dipotassium sodium cobaltinitrite, $K_2Na[Co(NO_2)_6],H_2O$. By precipitation of potassium solutions with sodium cobaltinitrite reagent under the experimental conditions given below, a quantitative yield of dipotassium sodium cobaltinitrite is obtained. This method, unlike the perchlorate procedure, is applicable in the presence of sulphate.

A. Determination of potassium as chloroplatinate. *Procedure.* Weigh out accurately about 0·25 g. of the mixed sodium and potassium chlorides (1) into a small porcelain dish, and dissolve it in 5 to 10 ml. of water. Treat with sufficient chloroplatinic acid reagent (2) to react completely with both the sodium and potassium. The necessary amount to use is readily calculated by assuming that the mixed chlorides are wholly sodium chloride-1·7 ml. of the reagent will precipitate 0·1 g. of sodium chloride. The dilution of the resultant solution should be such that when heated on the water bath, any precipitate that may have formed dissolves completely; this is to prevent occlusion of mother liquor in a mass of crystals suddenly formed. Evaporate nearly to dryness on the water bath, *i.e.*, until the solution is syrupy but solidifies on cooling. (Complete evaporation to dryness will dehydrate the sodium salt and render it less soluble in alcohol.) Add 10 ml. of 80 per cent (by volume) ethyl alcohol (3) to the cold dish, and break up the mass of crystals into a fine powder by means of a stirring rod having a flattened end. Decant the supernatant liquid through a weighed sintered glass or porous porcelain crucible (4). Repeat this treatment with 2 ml. portions of 80 per cent alcohol, grinding up the precipitate thoroughly each time, until the alcohol runs through entirely colourless and the residue is golden-yellow in colour; an orange-red colour indicates incomplete removal of the sodium salt. Transfer the residue to the filter crucible with the aid of a little 80 per cent alcohol, and drain off most of the alcohol. Dry at 135°C to constant weight: the crucible should be covered to avoid loss by decrepitation. Weigh as $K_2[PtCl_6]$.

Notes. 1. For practice in this procedure, the student may employ either A.R. potassium chloride or an artificial mixture of, say, equal weights of A.R. sodium and potassium chlorides.

2. The **chloroplatinic acid reagent** is **prepared** by dissolving 1 g. of chloroplatinic acid in 10 ml. of water.

3. This may be prepared by mixing 5 volumes of 95 per cent alcohol with 1 volume of water.

4. All washings must be kept, and the platinum contained in them subsequently recovered.

Weighing of potassium chloroplatinate as metallic platinum. As a check on the result obtained by the above method, the amount of platinum contained in the precipitate may be determined. Dissolve the precipitate by pouring hot water over it, and transfer the filtrate and washings quantitatively to a small beaker. Add 2 ml. of concentrated hydrochloric acid, followed by approximately 0·5 g. of magnesium ribbon (previously washed with water). Stir the solution, and hold the ribbon at the bottom of the beaker by means of a glass rod with a flattened end. When the magnesium has nearly disappeared, add a few ml. of dilute hydrochloric acid, and allow the platinum to settle. If the reduction is complete, the liquid is clear and colourless. To make sure add a little more magnesium, and note whether the solution darkens. Add dilute hydrochloric acid, boil to dissolve any basic salts which may be present, collect the platinum on a small filter paper, wash with water until free from chlorides, and ignite in a a weighed porcelain or, preferably, platinum crucible to constant weight. Weigh the platinum, and calculate the potassium equivalent by the proportion $Pt \equiv 2K$.

B. Determination of potassium as perchlorate. *Procedure.* Weigh out accurately about 0·3 g. of the mixed chlorides (1) into a small Pyrex or platinum dish, and dissolve it in 5 to 10 ml. of water. Add 5 ml. of 20 per cent perchloric acid solution, evaporate to dryness on the steam bath, and then heat carefully over a small flame (or upon a low temperature hot plate, $\not>$ 350°C) until thick white fumes of perchloric acid appear. Allow to cool, wash down the walls of the dish with a little water (5 to 10 ml.), add a further 5 ml. of 20 per cent perchloric acid solution, and repeat the evaporation to ensure complete conversion of the chlorides into the perchlorates. Continue the second evaporation until the contents of the dish are *almost dry*, so as to eliminate all the perchloric acid.

Allow to cool. When cold, and not before (2), stir the contents of the dish with 15 ml. of the special wash liquid (3). Decant the supernatant liquid through a weighed filter crucible (Gooch, sintered glass or porous porcelain). Repeat this with two 5 ml. portions of the wash liquid. Transfer the precipitate quantitatively to the crucible with the aid of the wash liquid. (About 50 ml. should suffice for the washing and the transfer of the precipitate.) Dry at 130°C for 1 hour, and weigh as $KClO_4$.

Notes. 1. For practice in this estimation, use either 0·3 g. of A.R. potassium chloride or a mixture of, say, equal weights of A.R. potassium and sodium chlorides.

2. On no account should the alcohol-perchlorate mixture be heated as a dangerous explosion may result. For danger attending the use of perchloric acid, see Section **IV, 70**.

3. The wash liquid consists of absolute alcohol containing 0·2 per cent of perchloric acid and saturated with potassium perchlorate. This may be prepared by adding 0·3 ml. of 60 per cent perchloric acid to 100 ml. of absolute ethyl alcohol, shaking this with excess of finely-powdered potassium perchlorate, and filtering through a dry filter paper.

B′. Note on the determination of potassium and sodium. If the mixture supplied consists of the sodium and potassium salts of volatile acids, it may be converted into the chlorides by several evaporations with hydrochloric acid in a Main-Smith crucible (compare Section **IV, 47A**). This will give the total chloride. The potassium is determined as the perchlorate as above, and therefrom the equivalent amount of potassium chloride is computed. The sodium chloride is obtained by difference.

D. Determination of potassium as dipotassium sodium cobaltinitrite. *Procedure.* **(Potassium in potassium sulphate.)** Weigh out accurately 0·1 g. of, say, A.R. potassium sulphate, dissolve it in 10 to 15 ml. of water, add 2 drops of glacial acetic acid, then excess (15 to 20 ml.) of the sodium cobaltinitrite reagent (1). Evaporate to dryness on the water bath. Wash the residue by decantation with 5 per cent acetic acid, then transfer it to a weighed sintered glass or porous porcelain crucible, and wash it with cold water until free from acid. Dry at 100°C to constant weight. Weigh as $K_2Na[Co(NO_2)_6],H_2O$. Calculate the percentage of potassium in potassium sulphate.

Note. 1. The **sodium cobaltinitrite reagent** is **prepared** as follows. Dissolve 22 g. of sodium nitrite in 40 ml. of water and add to it a solution containing 11·3 g. of cobalt acetate dissolved in 30 ml. of water and 10 ml. of glacial acetic acid. Gently warm the mixture, remove the nitrous fumes which are evolved by evacuation at the pump, and, after standing for 24 hours, filter off the small amount of yellow precipitate (due to the presence of potassium as impurity), and make up the solution to 100 ml. Keep in a dark place.

IV, 49. LITHIUM

Discussion. Lithium, if present as a salt of a volatile acid, may be determined as **lithium sulphate, Li_2SO_4** by repeated evaporation with sulphuric acid (see Section **IV, 47A**). No other elements may be present. Here the change from the acid sulphate to the normal sulphate takes place comparatively easily so that the addition of ammonium carbonate is not essential.

When present with sodium and potassium as chlorides, the lithium may be determined :

(*a*) by the *n*-butyl alcohol-ethyl acetate method (Section **IV, 48B**) ;

(*b*) by extraction of the lithium chloride with dry pyridine, amyl alcohol, dioxan (diethylene oxide) or anhydrous acetone, sodium and potassium chlorides being sparingly soluble in these solvents. The best separation is achieved by the use of dioxan or anhydrous acetone. The solubility of lithium chloride in dioxan is 2·80 g. per litre at 100°C, and 38·6 g. per litre at 25°C in anhydrous acetone. The solubility of sodium and potassium chlorides in these solvents is negligible. The method utilising dioxan will be described.

Determination of lithium in the presence of sodium and potassium. *Procedure.* Heat the mixed alkali chlorides at 120°C in a sintered glass crucible for 2 hours, and weigh after cooling in a desiccator. Suspend the crucible by means of platinum wires about 1 cm. above 20 to 30 ml. of pure dry dioxan contained in a wide-mouthed 250 ml. flask, which is attached to a reflux condenser having a calcium chloride guard tube at the top. Reflux for at least 4 hours, remove the crucible, heat at 120°C for 1 hour, cool, and weigh. Repeat the process until the weight is constant. The loss in weight is due to the lithium chloride.

IV, 50. AMMONIUM

Discussion. For the determination of ammonium by a gravimetric procedure, it must be present as the chloride ; all other cations must be absent. A little hydrochloric acid is added, followed by excess of chloroplatinic acid reagent (see Section **IV, 48A**). The mixture is evaporated almost to dryness on the water bath ; the residue is triturated with absolute alcohol to remove excess of chloroplatinic acid, and then transferred to a weighed filter crucible (Gooch, sintered glass or porous porcelain). The crucible is dried at 130°C, and the residual **ammonium chloroplatinate, $(NH_4)_2PtCl_6$** weighed. (For details of experimental procedure, see Section **IV, 48A.**)

If the ammonium salt is present with other cations and anions, a volumetric procedure (see Chapter III) is usually employed.

IV, 51. TUNGSTEN

Discussion. Tungsten, as tungstate, may be determined in one of the following forms:

A. Tungsten trioxide, WO_3, after precipitation with benzidine. Benzidine forms a white sparingly soluble tungstate with solutions of tungstates. The precipitate is, however, filtered with difficulty, and may tend to peptise during the washing process. If a little sulphuric acid is present, the slightly soluble and crystalline benzidine sulphate is also formed. This renders filtration facile. Upon igniting the mixture of benzidine tungstate and sulphate, only tungstic oxide remains.

B. Tungsten trioxide, WO_3, after precipitation with tannin and antipyrine. Tungstic acid is incompletely precipitated from solutions of tungstates by tannin. If, however, antipyrine is added to the cold solution after treatment with excess of tannin, precipitation is quantitative. This process effects a separation from aluminium, and also from iron, chromium, manganese, zinc, cobalt and nickel if a double precipitation is used.

For the use of cinchonine in the determination of tungsten, see Section **IV, 92, I.**

C. Tungsten "oxinate," $WO_2(C_9H_6ON)_2$. This method is applicable only when all other elements precipitable by oxine in acetic acid solution are absent.

A. Determination of tungsten as the trioxide (benzidine method). *Procedure.* The solution of the tungstate (200 ml.) should contain about 0·3 g. of WO_3, and be almost neutral (1). Add 10 ml. of 0·1N sulphuric acid, and boil the solution. Introduce immediately 30 ml. of the benzidine reagent (2), and allow to cool to room temperature. Filter through a weighed silica Gooch or porous porcelain crucible, and wash with a solution prepared by diluting 10 ml. of the reagent to 300 ml. Dry the precipitate, and ignite. Weigh as WO_3.

Notes. 1. For practice in this estimation, a solution prepared from A.R. sodium tungstate may be employed.

2. The reagent is prepared by dissolving 2 g. of A.R. benzidine in 100 ml. of 1 per cent hydrochloric acid.

B. Determination of tungsten as the trioxide (tannin-antipyrine method). *Procedure.* The solution of tungstate (200 to 250 ml.) should contain not more than 0·15 g. of WO_3, and be faintly ammoniacal. Add 6 to 7 ml. of concentrated sulphuric acid and 7 to 8 g. of ammonium sulphate, and heat to boiling. Treat with 6 ml. of 10 per cent tannin solution, keep the mixture on the water bath for a few minutes, and allow to cool to room temperature. A flocculent dark-brown precipitate separates. When cold, stir in 10 ml. of a 10 per cent solution of antipyrine ("phenazone"). Filter the precipitate through a weighed silica Gooch or porous porcelain crucible (1), wash with the special wash liquid (2), and ignite to constant weight. Weigh as WO_3.

Notes. 1. The filtrate must be colourless. If it is yellow, insufficient antipyrine has been added.

2. The special wash liquid contains 1 ml. of concentrated sulphuric acid, 10 g. of ammonium sulphate, and 0·4 g. of antipyrine in 200 ml. of water.

C. Determination of tungsten with oxine. *Procedure.* The solution of tungstate (200 ml.) should contain about 0·05 g. of W, and be slightly alkaline or neutral in reaction ; if acid, precipitation is subsequently effected with ammonium acetate. Heat to boiling, add a 4 per cent alcoholic solution of oxine slowly and with constant stirring until present in slight excess, and acidify with dilute acetic acid. Filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain). Wash with hot water, and dry at 120°C to constant weight. Weigh as $WO_2(C_9H_6ON)_2$.

IV, 52. CHLORIDE

Discussion. This anion is determined as **silver chloride, AgCl** ; full details are given in Section **IV, 5.** Anions which give silver salts which are insoluble in dilute nitric acid must be absent ; these include bromide, iodide, thiocyanate, sulphide, thiosulphate, ferrocyanide and ferricyanide. Heavy metals interfere, and must be removed by precipitation.

If the chloride is insoluble, it is necessary to boil it with a large excess of saturated sodium carbonate solution or, better, to fuse it with sodium carbonate and extract the melt with water. In either case the chloride passes into solution, and is estimated in the usual way after acidification with nitric acid.

IV, 53. BROMIDE

Discussion. This anion is determined as **silver bromide, AgBr** by precipitation with silver nitrate solution in the presence of dilute nitric acid. Silver bromide is less soluble in water than is the chloride. The solubility of the former is 0·11 mg. per litre at 21°C as compared with 1·54 mg. per litre for the latter, hence the procedure for the determination of bromide is practically the same as that for chloride. Protection from light is even more essential with the bromide than with the chloride because of its greater sensitiveness.

IV, 54. IODIDE

Discussion. This anion is usually determined by precipitation as **silver iodide, AgI.** Silver iodide is the least soluble of the silver halides ; 1 litre of water dissolves 0·0035 mg. per litre at 21°C.

Coprecipitation and similar errors are more likely to occur with iodide than with the other halides. Precipitation is therefore made by adding a very dilute solution, say 0·05*N*, of silver nitrate slowly and with constant stirring to a dilute ammoniacal solution of the iodide until precipitation is complete, and then adding nitric acid in 1 per cent by volume excess. The precipitate is collected in the usual manner, washed with 1 per cent nitric acid, and finally with a *little* water to remove nitric acid. Peptisation tends to occur with excess of water. Other details of the estimation will be found in Section **IV, 5.**

Iodide may also be determined by precipitation as **palladous iodide, PdI_2.** Substances, such as alcohol, which cause reduction to metallic palladium must be absent; bromides and chlorides are not precipitated and therefore do not interfere. The precipitate is insoluble in water and in dilute hydrochloric acid (1 : 99). The reagent, palladous chloride, is expensive, and the method is therefore rarely employed except for gravimetric separations from other halides.

Determination of iodide as palladous iodide. *Procedure.* The iodide solution should contain 1 per cent by volume of hydrochloric acid, and not more than 0·1 g. of iodide. Warm to 70°C, and add palladous chloride solution, dropwise and with stirring, until no more precipitate is formed. Allow the solution to stand for 24 to 48 hours at 20° to 30°C, filter the brownish-black precipitate of palladous iodide on a weighed filter crucible (Gooch, sintered glass or porous porcelain), and wash 4 times with warm water. Dry at 100°C for 1 hour, and weigh as PdI_2.

IV, 55. THIOCYANATE

This anion may be determined in one of the following forms:

A. Silver thiocyanate, AgCNS. This method is applicable only in the absence of halides and cyanides. The dilute solution of alkali thiocyanate is acidified with dilute nitric acid and treated in the cold with a slight excess of 0·1*N* silver nitrate. After stirring well, the precipitate is collected on a weighed filter crucible (Gooch, sintered glass or porous porcelain), washed with water followed by a little alcohol, and dried to constant weight at 130°C. The precipitate is weighed as AgCNS.

B. Cuprous thiocyanate, $Cu_2(CNS)_2$. The solution (100 ml.) should be neutral or slightly acid (hydrochloric or sulphuric acid), and contain not more than 0·1 g. CNS. It is saturated with sulphur dioxide in the cold (or 50 ml. of freshly-prepared saturated sulphurous acid solution added), and then treated dropwise and with constant stirring with about 60 ml. of about 0·1*N* copper sulphate. The mixture is again saturated with sulphur dioxide (or 10 ml. of saturated sulphurous acid solution added), allowed to stand for a few hours, collected on a weighed filter crucible (Gooch, sintered glass or porous porcelain), washed several times with cold water containing sulphurous acid until the copper is removed (potassium ferrocyanide test), and finally once with alcohol. The precipitate is dried at 110° to 120°C to constant weight, and weighed as $Cu_2(CNS)_2$.

C. Barium sulphate, $BaSO_4$. The thiocyanate is oxidised with bromine water to sulphate, and the latter is determined by precipitation as barium sulphate. All other compounds containing sulphur must be absent. The alkali thiocyanate solution is treated with excess of bromine water, heated for 1 hour on the water bath, the solution acidified with hydrochloric acid, and the sulphuric acid precipitated and weighed as $BaSO_4$ (see Section **IV, 6**).

IV, 56. CYANIDE

Discussion. This anion is determined as **silver cyanide, AgCN**; the experimental details are similar to those given for Chloride except that, owing to the volatility of hydrocyanic acid, the solution must not be heated. The cold solution of alkali cyanide is treated with an excess of silver nitrate solution, faintly acidified with nitric acid, the precipitate allowed to settle, collected on a weighed filter crucible, and weighed as AgCN after drying at 110°C.

IV, 57. FLUORIDE

Discussion. This anion may be determined in one of the following forms :

A. Lead chlorofluoride, PbClF. The details of this procedure are given in Section **III, 39.** The precipitate is, however, filtered through a weighed filter crucible (Gooch, sintered glass or porous porcelain), and weighed as PbClF after drying at 130° to 140°C.

B. Calcium fluoride, CaF_2. Fluorides, in the absence of phosphates, silicates and other radicals that give insoluble calcium salts, may be determined as calcium fluoride by precipitation with calcium chloride solution. The precipitate produced in acid or neutral solution is gelatinous and difficult to filter. For this reason a little sodium carbonate solution is often added before precipitation ; the precipitate of calcium fluoride and calcium carbonate is more readily filtered. The calcium carbonate is subsequently removed by extraction with dilute acetic acid. A simpler procedure is to carry out the precipitation in ammoniacal solution ; the resultant calcium fluoride is much denser, and comparatively easily filtered and washed.

C. Triphenyltin fluoride, $(C_6H_5)_3SnF$. Triphenyltin chloride reagent precipitates fluorides quantitatively as the corresponding fluoride. The precipitate is crystalline, easily filtered and quickly washed, and is quite stable. Owing to the insolubility of the reagent in water, precipitation is carried out in 60 to 70 per cent alcoholic solution and washing is effected with an alcoholic solution of the reagent saturated with triphenyltin fluoride.

The conversion factor is particularly small (0·05149), so that the method is well adapted for the estimation of small quantities of fluorides. The maximum amount that can be conveniently handled is 0·04 g. of F. The solution should have a *p*H of 5 to 7 ; if acid some fluorine will be lost on heating to boiling, and if basic triphenyltin hydroxide will be precipitated along with the fluoride. Metals other than those of the alkalis should preferably be absent ; the alkali metals may be removed by washing the precipitate several times with the alcohol wash solution, followed by cold water. Small quantities of nitrates, chlorides, bromides, iodides and sulphates do not interfere, but silicates (with ammoniacal zinc hydroxide), phosphates (with silver nitrate) and carbonates must be removed before precipitation. Carbonate is best removed by neutralising with dilute nitric acid (to phenolphthalein), and boiling off the carbon dioxide. A disadvantage of the method is that the reagent is expensive.

B. Determination of fluoride as calcium fluoride. *Procedure.* The alkali fluoride solution should have a volume of 75 to 100 ml., and contain up to 0·3 g. of F. Add 7 ml. of concentrated ammonia solution and 20 ml. of 0·5*M* calcium chloride in the cold, slowly and with stirring. Boil the solution for 1 to 2 minutes, allow the precipitate to settle, and decant the mother liquor through a quantitative filter paper. Add 20 ml. of water and 1 ml. of concentrated ammonia solution, boil, and decant as before : repeat the process. Transfer the precipitate to the filter, and wash 3 to 4 times with hot water. Place the filter and precipitate in a weighed Main-Smith crucible, burn off the filter paper, and ignite at 500° to 600°C (dull red heat) to constant weight. Weigh as CaF_3. As an additional check, convert the calcium fluoride into calcium sulphate by two or three evaporations with concentrated sulphuric acid, ignite at about 500°C and weigh as $CaSO_4$; if this is carried out, the initial ignition must be carried out in a platinum crucible.

C. Determination of fluoride as triphenyltin fluoride. *Procedure.* The solution (say, 25 ml.) should contain not more than 0·04 g. of F, and be almost neutral (1). Add 95 per cent ethyl alcohol to the aqueous solution of the fluoride so that it comprises about 60 to 70 per cent of the final volume. Heat to boiling and treat with twice the calculated quantity of the reagent (2) diluted with an equal volume of 95 per cent alcohol and also heated to boiling. The latter is run slowly into the hot fluoride solution with vigorous stirring, and the whole again heated to the boiling point. Remove the source of heat, and continue the stirring until the solution has cooled somewhat (3). Allow to stand overnight, and cool for 1 hour in ice (4). Filter through a weighed sintered glass or porous porcelain crucible, wash with 95 per cent ethyl alcohol which has been saturated with triphenyltin fluoride (about 50 ml.). Dry for 30 minutes at 110°C, cool in a desiccator, and weigh as $(C_6H_5)_3SnF$.

Notes. 1. For practice in this estimation, A.R. sodium fluoride (obtainable from the Mallinckrodt Chemical Works, U.S.A. ; see, however, Appendix, Section **A, 9**) may be used. If desired, a sample of *pure sodium fluoride* may be prepared as follows. Treat A.R. anhydrous sodium carbonate with an excess of A.R. hydrofluoric acid in a platinum dish, and allow to stand for a few hours. Remove the excess of acid by heating (fume cupboard), allow to cool, and add more acid. Mix thoroughly with a platinum spatula, heat the dish gently at first, and then strongly until the sodium fluoride is entirely fused. Pulverise in an agate mortar, dry the powder in platinum at 110°C, and store in a desiccator over calcium chloride.

2. The reagent is prepared by shaking vigorously 4·0 g. of triphenyltin chloride (obtainable from the Eastman Kodak Co.) with 200 ml. of 95 per cent ethyl alcohol ; filter from the small undissolved residue. This is practically a saturated solution.

About 55 ml. of this reagent are required for 0·04 g. F.

3. If the quantity of fluoride is large, precipitation commences in about a minute after the addition of the reagent as white crystals, but with small quantities it does not take place until the solution has cooled to room temperature.

4. This is unnecessary if the amount of fluoride is large and the total volume of the solution small.

IV, 58. CHLORATE

Discussion. The chlorate is reduced to chloride, and the latter is determined as **silver chloride, AgCl.** The reduction may be performed with ferrous sulphate solution, sulphur dioxide or zinc. Alkali chlorates may be quantitatively converted into chlorides by three evaporations with concentrated hydrochloric acid, or by evaporation with three times the weight of ammonium chloride ; the operations are conveniently carried out in a Main-Smith crucible (Section **II, 36B**).

Determination of chlorate as silver chloride. *Procedure.* The chlorate solution should have a volume of about 100 ml., and contain about 0·2 g. of ClO_3. Add 50 ml. of a 10 per cent solution of A.R. crystallised ferrous sulphate, heat with constant stirring to the boiling point, and maintain the boiling for 15 minutes. Allow to cool, add nitric acid until the precipitated basic ferric salt is dissolved, precipitate the chloride by means of silver nitrate solution, and collect and weigh as AgCl after the usual treatment (Section **IV, 5**).

Alternatively, treat the chlorate solution with excess of sulphur dioxide, boil the solution to remove the excess of the gas, render slightly acid with nitric acid, and precipitate the silver chloride as above.

For the reduction with zinc, render the chlorate solution strongly acid with acetic acid, add excess of zinc, and boil the mixture for 1 hour. Dissolve the excess of unused zinc with nitric acid, filter, and treat the filtrate with silver nitrate in the usual manner.

Note. **Hypochlorites** and **chlorites** may be reduced to chlorides with sulphur dioxide, and determined in the same way.

IV, 59. PERCHLORATE

Discussion. Perchlorates are not reduced by ferrous sulphate solution, sulphurous acid or by repeated evaporation with concentrated hydrochloric acid ; reduction occurs, however, with titanous sulphate solution. Ignition of perchlorates with ammonium chloride in a platinum crucible or in a porcelain crucible in the presence of a little platinum powder results in reduction to the chlorides (the platinum acts as a catalyst), which may be determined in the usual manner. Losses occur when perchlorates are ignited alone.

Perchlorates may also be determined as **potassium perchlorate, $KClO_4$**. Sodium perchlorate is estimated directly by precipitation with concentrated potassium acetate solution. The sparingly soluble perchlorates of the heavy metals are first precipitated with excess of sodium carbonate solution, filtered, and the filtrate (containing sodium perchlorate) evaporated to dryness on the water bath. The cold residue is extracted six times with 5 ml. portions of absolute alcohol, and the filtrate carefully evaporated on the water bath. It is essential that the alcoholic solution be neutral or alkaline in reaction, otherwise a dangerous explosion may result upon evaporation. The residue is dissolved in 20 ml. of water, and precipitated as $KClO_4$ with potassium acetate solution.

A. Determination of perchlorate as silver chloride.

Procedure. The perchlorate, if in the form of a solution, is evaporated to dryness on the water bath ; otherwise the solid perchlorate is used directly. Intimately mix about 0·4 g. of the perchlorate (1) with 1·5 g. of A.R. ammonium chloride in a *platinum* crucible covered with a watch glass or lid, ignite gently until fuming ceases and continue the heating for 1 hour. Do not fuse the resultant chloride, as the crucible may be attacked. Repeat the ignition with another 1·5 g. of ammonium chloride. Dissolve the residue in a little water, filter through a small quantitative filter paper to remove any platinum powder which may be present, and estimate the chloride in the filtrate as silver chloride (Section **IV, 5**).

Note. 1. For practice in this estimation, the student may employ A.R. potassium perchlorate.

B. Determination of perchlorate as potassium perchlorate. *Procedure.* The perchlorate solution should be in the form of the sodium salt (see *Discussion* above), have a volume of about 25 ml., and contain about 0·4 g. of ClO_4. Warm the solution to 80° to 90°C, and treat with a slight excess of a cold saturated solution of potassium acetate. Allow the solution to cool, and after 1 hour collect the precipitate on a weighed filter crucible (Gooch, sintered glass or porous porcelain). Wash twice with 0·05*M* potassium acetate, then 4 times with absolute alcohol (1), and draw air through the precipitate until it appears dry. Dry at 110°C to constant weight, and weigh as $KClO_4$.

Note. 1. It is preferable to use the special wash liquid described in Section **IV, 48B,** Note 3.

IV, 60. IODATE

Discussion. Iodates are readily reduced by sulphurous acid to iodides; the latter are determined by precipitation with silver nitrate solution as **silver iodide, AgI.** Iodates cannot be converted quantitatively into iodides by ignition, for the decomposition takes place at a temperature at which the iodide is appreciably volatile.

Periodates are also reduced by sulphurous acid, and may therefore be similarly determined. Similar remarks apply to **bromates**; these are ultimately weighed as silver bromide, AgBr.

Determination of iodate as silver iodide. *Procedure.* Acidify the iodate solution (100 ml. containing *ca.* 0·3 g. of IO_3) (1) with sulphuric acid, and pass in sulphur dioxide (or add a freshly-prepared saturated solution of sulphurous acid) until the solution which at first becomes yellow, on account of the separation of iodine, is again colourless. Boil off the excess of sulphur dioxide, and precipitate the iodide with dilute silver nitrate solution as described in Section **IV, 54.** Weigh as AgI.

Note. 1. For practice in this determination, the student may employ A.R. potassium iodate.

IV, 61. SULPHATE

Discussion. Full details for the determination of soluble sulphates as **barium sulphate, $BaSO_4$** are given in Section **IV, 6.** For sulphates which are insoluble in water and acids, it is best to mix the finely-powdered solid with 6 to 12 times its bulk of anhydrous sodium carbonate in a platinum crucible set in an asbestos shield (Section **II, 38**), heat the covered crucible slowly to fusion, and maintain in the fused state for 15 minutes. The melt is extracted with water, the solution filtered, the residue washed with hot 1 per cent sodium carbonate solution, and the cold filtrate carefully acidified with hydrochloric acid (to methyl orange). The sulphate is determined as in Section **IV, 6.** If silica is present, the acid filtrate is evaporated to dryness on the water bath to dehydrate the silica; a little concentrated hydrochloric acid is added, followed by hot water. The silica is filtered off, and the sulphate determined in the filtrate.

A **comparatively rapid method for the determination of sulphate,** which is particularly suitable for routine estimations, is based upon the precipitation as $BaSO_4$ in the presence of picric acid (C. H. Lindlsly, 1936). Prolonged digestion (compare Section **IV, 6**) is unnecessary, and the solution may be filtered after about 10 minutes. The detailed procedure is as follows. The slightly acidified sulphate solution is treated with 1 to 5 ml. of saturated picric acid solution according to the sulphate content (1), a slight excess of barium chloride solution is added rapidly (2), and the solution gently boiled for 5 to 10 minutes. The precipitate may then be filtered off, thoroughly washed, and weighed as in Section **IV, 6.**

Notes. 1. If large amounts of sodium salts are present, 10 to 25 ml of the saturated picric acid solution are necessary.

2. In this method there is no advantage in adding the barium chloride solution slowly.

IV, 62. SULPHIDE

Discussion. The determination of sulphur in insoluble sulphides by wet and dry processes and subsequent weighing as **barium sulphate, $BaSO_4$,** is fully dealt with in Section **IV, 7.** Other methods, which are particularly applicable to soluble sulphides, include oxidation in alkaline solution with sodium hypochlorite or hydrogen peroxide,* followed by the estimation of sulphate as barium sulphate.

IV, 63. SULPHITE

Discussion. Sulphites may be readily converted into sulphates by boiling with excess of bromine water, sodium hypochlorite, sodium hypobromite or ammoniacal hydrogen peroxide (equal volumes of 20-volume hydrogen peroxide and 1 : 1 ammonia solution). The excess of the reagent is decomposed by boiling, the solution acidified with hydrochloric acid, precipitated with barium chloride solution, and the **barium sulphate** collected and weighed in the usual manner (Section **IV, 6**).

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*Ammoniacal hydrogen peroxide is usually employed. The hydrogen peroxide must be free from sulphate.

IV, 64. THIOSULPHATE

Discussion. Thiosulphates are oxidised to sulphate by methods similar to those described for sulphites (Section **IV, 63**). The sulphate is then determined as **barium sulphate.** One molecule of thiosulphate corresponds to two molecules of barium sulphate.

IV, 65. PHOSPHATE

Discussion. Orthophosphates may be precipitated as **magnesium ammonium phosphate, $MgNH_4PO_4,6H_2O$,** by magnesium chloride and ammonium chloride in ammoniacal solution (" magnesia " reagent). Most elements, other than those of the alkalis, interfere, however, by giving precipitates with " magnesia mixture." It is therefore necessary in the majority of cases to separate the phosphate first from interfering substances. This may be readily effected by precipitation as **ammonium phosphomolybdate, $(NH_4)_3PO_4,12MoO_3,2HNO_3,H_2O$,** with excess of ammonium molybdate in warm nitric acid solution : arsenic, vanadium, titanium, zirconium, silica, and excessive amounts of ammonium salts interfere. The precipitate thus obtained is dissolved in dilute ammonia solution, and the phosphate is then precipitated as magnesium ammonium phosphate. A double precipitation of the latter is necessary in order to obtain a precipitate entirely free from molybdate.

If interfering elements are absent, the original precipitate of ammonium phosphomolybdate may be weighed as **phosphomolybdic anhydride, $P_2O_5,24MoO_3$,** after gentle ignition. For practice in this simple estimation, the student may determine the percentage of phosphate in anhydrous A.R. sodium phosphate, Na_2HPO_4. (Most of the experimental details are given in Section **III, 146.**) The precipitate of ammonium phosphomolybdate should, however, be filtered through a weighed Gooch or porous porcelain crucible, and washed with the special wash liquid (1) until only a faint brown colour is given when 5 ml. of the washings are tested with potassium ferrocyanide solution. The precipitate is dried at 280° to 300°C (electric oven) to constant weight. Alternatively, the precipitate is dried in the steam oven, then placed in a larger nickel crucible resting upon a pad of ignited asbestos, 2 mm. thick, covering the bottom of the crucible ; the asbestos may be replaced by a porcelain plate of a Gooch crucible, The filter crucible is covered with a watch glass, and the nickel crucible gradually heated until the bottom is at a dull red heat. In either case, when the precipitate has acquired a homogeneous bluish-black colour, it is allowed to cool in a desiccator (it is appreciably hygroscopic), and weighed as $P_2O_5,24MoO_3$.

Note. 1. Prepared by dissolving 10 g. of ammonium nitrate in water, adding 8 ml. of concentrated nitric acid, and diluting to 200 ml.

A. Determination of phosphate as magnesium pyrophosphate. *Procedure.* To a neutral or weakly acid solution (50 to 100 ml.) of the phosphate, containing not more than 0·1 g.

of P_2O_5 and free from interfering elements (1), add 3 ml. of concentrated hydrochloric acid and a few drops of methyl red indicator. Introduce 25 ml. of magnesia mixture (Section **IV, 20B,** Note 2), followed by pure concentrated ammonia solution slowly whilst stirring the solution vigorously until the indicator turns yellow. The procedure from this stage is the same as described for the determination of Magnesium in Section **IV, 11,** except that when carrying out the reprecipitation from the hydrochloric acid solution 2 ml. of the magnesia mixture are added instead of the 1 ml. of ammonium phosphate solution. Weigh as $Mg_2P_2O_7$.

Note. 1. A suitable solution for practice may be prepared by dissolving about 0·4 g., accurately weighed, of A.R. anhydrous Na_2HPO_4 in 100 ml. of water.

B. Determination of phosphate as magnesium pyrophosphate after a preliminary separation as ammonium phosphomolybdate. *Procedure.* For practice in this estimation, it is recommended that basic slag (1) be employed. Weigh out accurately about 2·5 g. of the finely-powdered basic slag into a 10 cm. porcelain or Pyrex basin. Add 20 ml. of concentrated sulphuric acid, and mix to a smooth paste. Heat the mixture on a sand bath (or hot plate) in the fume cupboard until white fumes begin to appear, and then keep it in this condition for 45 minutes with stirring at intervals. Avoid strong fuming of the sulphuric acid. Allow to cool, dilute carefully with water, and, when cold, filter into a 250 ml. volumetric flask, wash the residue thoroughly with cold water, and make up to the mark. Measure out 50 ml. of the solution (do not allow the solution to stand too long as calcium sulphate is liable to crystallise out) into a 400 ml. beaker, add 10 ml. of concentrated nitric acid, followed by 1 : 1-ammonia solution until a faint permanent precipitate appears. Redissolve the precipitate by the addition of a few drops of concentrated nitric acid, heat to 40° to 45°C (use thermometer), and treat with 100 ml. of the ammonium molybdate reagent (Section **III, 146**) previously heated to the same temperature, slowly and with stirring ; continue the stirring for about 10 minutes. Allow the precipitate to stand for a few hours, but preferably overnight. Filter through a Whatman No. 40 or No. 540 filter paper, leaving as much as possible of the precipitate in the beaker, and wash the precipitate moderately with 5 per cent ammonium nitrate solution. Pour 10 ml of 1 : 2 ammonia solution dropwise on to the paper to redissolve the precipitate, wash with water, and collect the filtrate and washings in the original beaker which contains the bulk of the precipitate. Render the ammoniacal solution slightly acid (methyl red) with dilute hydrochloric acid, and introduce 25 ml. of magnesia mixture (Section **IV, 20B,** Note **2**) dropwise and stirring continuously. Next add 10 to 15 ml. of 1 : 1 ammonia solution slowly and with stirring. Allow the solution to stand for at least 4 hours, but preferably overnight. Filter, without attempting to transfer the precipitate, wash the vessel, residue and paper a few times with 1 : 20 ammonia solution. Dissolve the precipitate on the filter in 25 ml. of 1 : 1 hydrochloric acid, and collect the solution in the original beaker containing the bulk of the precipitate. Wash the filter paper thoroughly with warm 1 : 20 hydrochloric acid. Add to the filtrate and washings, diluted to 100 ml., 2 ml. of magnesia mixture ; then reprecipitate the phosphate by the addition of 1 : 1 ammonia solution drop by drop and with thorough stirring, and finally add 10 ml. of the 1 : 1 ammonia solution in excess. Allow to stand for 12 hours. Collect the precipitate on a filter paper or in a weighed silica Gooch or porous porcelain crucible, and wash with cold 1 : 20 ammonia solution. Complete the determination as described in Section **IV, 11,** and weigh as $Mg_2P_2O_7$.

Note. 1. Ridsdale's " Basic Slag (Thomas Phosphate), No. 31 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Basic Slag ' A ' " (one of the British Chemical Standards) is suitable.

IV, 66. PHOSPHITE

Discussion. This anion may be determined in either of the following forms :

A. Mercurous chloride, Hg_2Cl_2. The acid solution of phosphite reduces mercuric chloride solution to calomel, which is weighed. The reaction is :

$$2HgCl_2 + H_3PO_3 + H_2O = Hg_2Cl_2 + H_3PO_4 + 2HCl,$$

whence $Hg_2Cl_2 \equiv H_3PO_3$.

B. Magnesium pyrophosphate, $Mg_2P_2O_7$. The phosphite is oxidised by nitric acid to phosphate, and the latter is determined as magnesium pyrophosphate.

A. Determination of phosphite as mercurous chloride.

Procedure. The phosphite solution (30 ml.) should contain about 0·1 g. of HPO_3^{--}. Place 50 ml. of 3 per cent mercuric chloride solution, 20 ml. of 10 per cent sodium acetate and 5 ml. of glacial acetic acid in a 250 ml. beaker, and add the phosphite solution dropwise, and with stirring, in the cold. Allow to stand on a water bath at 30° to 45°C for 2 hours.

When cold, filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain), wash 2 or 3 times with 1 per cent hydrochloric acid, and then 4 times with warm water. Dry at 100° to 105°C, and weigh as Hg_2Cl_2.

B. Determination of phosphite as magnesium pyrophosphate. *Procedure.* Treat the aqueous solution of the phosphite (100 ml.) with 5 ml. of concentrated nitric acid, evaporate to a small volume on the water bath, add 1 ml. of fuming nitric acid, and heat again. Dilute the solution, and precipitate the phosphoric acid by magnesia mixture and ammonia solution, and weigh as $Mg_2P_2O_7$ (Section **IV, 65A**).

IV, 67. HYPOPHOSPHITE

Discussion. This anion is determined similarly to phosphite either as **mercurous chloride, Hg_2Cl_2,** or as **magnesium pyrophosphate, $Mg_2P_2O_7$.** In this case the reaction with mercuric chloride solution is:

$$4HgCl_2 + H_3PO_2 + 2H_2O = 2Hg_2Cl_2 + H_3PO_4 + 4HCl,$$

so that $2Hg_2Cl_2 \equiv H_3PO_2$.

IV, 68. OXALATE

Discussion. The neutral solution of alkali oxalate is acidified with acetic acid, heated to boiling, and precipitated with boiling calcium chloride solution. After standing for 12 hours, the precipitate is filtered off, washed with hot water, and weighed either as **calcium carbonate, $CaCO_3$,** or as **calcium oxide, CaO** (for details, see Section **IV, 10**).

The following rapid method (J. Dick, 1929) yields results of moderate accuracy. Precipitation of the oxalate is effected in boiling solution containing a little ammonium chloride by a hot solution of calcium chloride. The solution is allowed to cool, treated with one-third of its volume of rectified spirit, and allowed to stand for 30 minutes. The precipitate is washed by decantation through a weighed porous porcelain or sintered glass crucible with warm water (50° to 60°C) until the chloride reaction is negative. The calcium oxalate is then transferred to the filter crucible, washed once with cold water, 5 times with rectified spirit, and several times with small volumes of anhydrous ether. The precipitate is sucked dry at the pump for 10 minutes, the outside of the crucible wiped dry with a clean linen cloth, and then left in a vacuum desiccator for 10 minutes. It is weighed as CaC_2O_4,H_2O.

IV, 69. BORATE

Discussion. The most trustworthy methods for the determination of borate are based upon its volatilisation as **methyl borate, $B(OCH_3)_3$**; this is achieved by acidifying the alkali or alkaline earth borates and heating with absolute methyl alcohol (methanol). The methyl borate is saponified and the boric acid fixed in a weighed amount of lime, which is again weighed after ignition : Alternatively, the boric acid is titrated after the addition of mannitol as described in Section **III, 17.** For complete details, the reader is referred to other treatises (1).

Note. 1. For example : W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis,* 1929, p. 611 ; J. W. Mellor and H. W. Thompson, *A Treatise on Quantitative Inorganic Analysis,* 1938, p. 659 ; W. D. Treadwell, *Tabellen und Vorschriften zur Quantitativen Analyse,* 1938, p. 174 ; G. E. F. Lundell, J. I. Hofmann and H. A. Bright, *Chemical Analysis of Iron and Steel,* 1931, p. 390.

IV, 70. SILICATE

Discussion. Silicates may be divided into two classes : (*a*) those (" soluble " silicates) which are decomposed by acids, such as hydrochloric acid, to form silicic acid and the salts (*e.g.*, chlorides) of the metals present, and (*b*) those (" insoluble " silicates) which are not decomposed by any acid, except hydrofluoric acid. There are also many silicates which are partially decomposed by acids ; for our purpose these will be included in class (*b*). Insoluble silicates are generally fused with sodium carbonate, and the melt, which contains the silicate in acid-decomposable form, is then treated with hydrochloric acid. The acid solution of the decomposed silicate is evaporated to dryness on the water bath to separate the gelatinous silicic acid SiO_2,xH_2O as insoluble silica SiO_2,yH_2O ; the residue is heated at 110° to 120° C to partially dehydrate the silica and render it as insoluble as possible. The residue is extracted with hot dilute hydrochloric acid to remove salts of iron, aluminium, and other metals which may be present. The greater portion of the silica remains undissolved, and is filtered off. The filtrate is evaporated to dryness, and the residue heated at 110° to 120°C as before in order to render insoluble the small amount of silicic acid that has escaped dehydration. The residue is treated with dilute hydrochloric acid as before, and the second portion of silica is filtered off on a fresh filter. The two washed precipitates are combined, and ignited in a platinum crucible at about 1000°C to **silicon dioxide, SiO_2**, and the latter is weighed. The ignited residue is not usually pure silicon dioxide ; it will generally contain small amounts of the oxides of iron, aluminium, titanium, etc. The amount of impurity may be determined, if desired, by treating the weighed residue in the platinum crucible with an excess of hydrofluoric acid and a little concentrated sulphuric acid. The silica is expelled as the volatile silicon tetrafluoride ; the impurities (*e.g.*, Al_2O_3 and Fe_2O_3) are first converted into the fluorides, which pass into the sulphates in contact with the less volatile sulphuric acid, whilst the subsequent ignition converts the sulphates back into oxides. Thus, for example:

$$SiO_2 + 6HF = H_2[SiF_6] + 2H_2O ; \quad H_2[SiF_6] = SiF_4 + 2HF ;$$
$$Al_2O_3 + 6HF = 2AlF_3 + 3H_2O ; \ 2AlF_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6HF ; \ Al_2(SO_4)_3 = Al_2O_3 + 3SO_3.$$

The loss in weight therefore represents the amount of pure silicon dioxide present.

Seventy per cent perchloric acid has been recommended for the dehydration of silicic acid. The solution, containing hydrochloric and nitric acid, is evaporated to strong fuming with excess of perchloric acid, and heated for a further 15 to 20 minutes; water is then added and the silica filtered off. A second evaporation is necessary for the filtrate to separate the small amount of dissolved silicic acid. The perchlorates of the metals, except that of potassium, are readily soluble so that the method possesses certain advantages. Organic compounds must, however, be absent, as dangerous explosions may result.

EXPLOSIVE DANGERS OF PERCHLORIC ACID.—*It must be emphasised that aqueous and anhydrous perchloric acids are powerful oxidising agents. In the presence of carbon and easily oxidisable organic compounds, a dangerous explosion may result on heating with the aqueous acid; in some cases explosion may result even in the cold with the aqueous acid. Evaporations with perchloric acid should be carried out in a fume cupboard, which is kept clean and free from combustible materials. The acid should be kept in a fire-proof store, and reasonable care should be taken in handling it.*

A. Determination of silica in a "soluble" silicate. *Procedure.* Weigh out accurately about 0·4 g. of the finely powdered silicate (1) into a platinum or porcelain dish, add 10 to 15 ml. of water, and stir until the silicate is thoroughly wet. Place the dish, covered with a clock glass or a Fisher "speedyvap" beaker cover, on the water bath, and add gradually 25 ml. of 1 : 1 hydrochloric acid. The contents of the dish must be continuously stirred with a glass rod; when no gritty particles remain, the powder will have been completely decomposed. Evaporate the liquid to dryness: stir the residue continuously and break up any lumps with the glass rod. When the powder appears to be dry, place the basin in an air oven at 110° to 120°C for 1 hour in order to dehydrate the silica. Moisten the residue with 5 ml. of concentrated hydrochloric acid, and bring the acid into contact with the solid with the aid of a stirring rod. Add 75 ml. of water, rinse down the sides of the dish, and heat on a steam bath for 10 to 20 minutes to assist in the solution of the soluble salts. Filter off the separated silica on a Whatman No. 41 or No. 541 filter paper. Wash the precipitate first with warm 1 : 20 hydrochloric acid, and then with hot water until free from chlorides. Pour the filtrate and washings into the original dish, evaporate to dryness on the steam bath, and heat in an air oven at 110° to 120°C for 1 hour. Moisten the residue with 5 ml. of concentrated hydrochloric acid, add 75 ml. of water, warm to extract soluble salts, and filter through a fresh, but smaller, filter paper. Wash with warm 1 : 100 hydrochloric acid, and finally with a little hot water. Fold up the moist filters, and place them in a weighed platinum crucible. Dry the paper with a small flame, char the paper, and burn off the carbon over a low flame (Section **II, 36**) ; take care that none of the fine powder is blown away. When all the carbon has been oxidised, cover the crucible, and heat for an hour at the full temperature of a Méker type of burner in order to complete the dehydration. Allow to cool in a desiccator, and weigh. Repeat the ignition, etc., until the weight is constant.

To determine the exact SiO_2 content of the residue, moisten it with 1 ml. of water, add 2 or 3 drops of concentrated sulphuric acid and about 5 ml. of the purest available (A.R.) hydrofluoric acid. Place the crucible in a radiator or air bath (Section **II, 13F**) and evaporate the hydrofluoric acid in a fume cupboard with a small flame until the acid is completely expelled ; the liquid should not be boiled. (The crucible may also be directly heated with a small luminous flame.) Then increase the heat to volatilise the sulphuric acid, and finally heat with a Méker type burner for 15 minutes. Allow to cool in a desiccator and weigh. Reheat to constant weight. The loss in weight represents the weight of the silica (2).

Notes. 1. For practice in this estimation, powdered fused sodium silicate may be used.

2. It is advisable to carry out a blank determination with the hydrofluoric acid, and to allow for any non-volatile substances, if necessary.

B. Determination of silica in an "insoluble" silicate. *Procedure.* Weigh out accurately into a platinum crucible about 1 g. of the finely-powdered dry silicate (1), add 6 times the weight of anhydrous A.R. sodium carbonate (or, better, of A.R. fusion mixture) and mix the solids thoroughly by stirring with a thin rounded glass rod. Cover the mixture with a little more of the carbonate, and then cover the crucible. Heat the mixture gradually until after about 20 minutes a tranquil melt is obtained ; the cover of the crucible is lifted occasionally to examine the contents. Maintain the temperature of a quiet liquid fusion for about 30 minutes. Allow to cool. Place the crucible and lid in a covered deep porcelain or platinum basin (or in a large casserole), cover it with water, and leave overnight, or warm on the water bath until the contents are well disintegrated. When this is the case, add very slowly about 20 ml. of concentrated hydrochloric acid by means of a pipette or bent funnel into the covered vessel. Warm on the steam bath until the evolution of carbon dioxide has ceased. Remove and rinse the cover glass, crucible and lid, and evaporate the contents of the dish to *complete* dryness on the steam bath, crushing all lumps with a glass rod. Heat the residue for an hour at 110° to 120°C to dehydrate the silica. Complete the estimation as described in **A.**

Note. 1. Ridsdale's "Felspar (Potash), No. 29" (one of the Analysed Samples for Students) is suitable.

IV, 71. FLUOSILICATE

Discussion. The determination of this anion is of little practical importance. The methods available for its estimation will, however, be outlined. Alkali fluosilicates are decomposed by heating with sodium carbonate solution into a fluoride and silicic acid :

$$Na_2[SiF_6] + 2Na_2CO_3 + H_2O = 6NaF + H_2SiO_3 + 2CO_2.$$

Insoluble fluosilicates are brought into solution by fusion with 4 times the bulk of fusion mixture, and extracting the melt with water. In either case, the solution is treated with a considerable excess of ammonium carbonate, warmed to 40°C, and, after standing for 12 hours, the precipitated silicic acid is filtered off, and washed with 2 per cent ammonium carbonate solution. The filtrate contains a little silicic acid, which may be removed by shaking with a little freshly precipitated cadmium oxide. The fluoride in the filtrate is determined as described in Section **IV, 57.**

If an acid solution of a fluosilicate is rendered faintly alkaline with aqueous sodium hydroxide and then shaken with freshly precipitated cadmium oxide, all the silicic acid is adsorbed by the suspension. The alkali fluoride is then estimated in the filtrate.

IV, 72. FERROCYANIDE

No satisfactory gravimetric procedure is available. Volumetric methods are described in Chapter III.

IV, 73. FERRICYANIDE

No satisfactory gravimetric method is available. For volumetric methods, see Chapter III.

IV, 74. NITRITE

No satisfactory gravimetric procedure is available. Volumetric methods are described in Chapter III.

IV, 75. NITRATE

Discussion. The mono-acid base nitron $C_{20}H_{16}N_4$ forms a fairly insoluble crystalline nitrate $C_{20}H_{16}N_4,HNO_3$, (solubility is 0·099 g. per litre at about 20°C) which can be used for the quantitative estimation of nitrates (see Section **I, 62, I**). The sulphate and acetate are soluble so that precipitation may be made in sulphuric or acetic acid solution. Perchlorates (0·08 g.), iodides (0·17 g., thiocyanates (0·4 g.), chromates (0·6 g.), chlorates (1·2 g.) nitrites (1·9 g.), bromides (6·1 g.), ferrocyanides, ferricyanides, oxalates, and considerable quantities of chlorides interfere and should be absent. The figures in parentheses are the approximate solubilities of the nitron salts in grams per litre at about 20°C.

Determination of nitrate as nitron nitrate. *Procedure.* The solution (75 to 100 ml.) should be neutral and contain about 0·1 g. of NO_3. Add 1 ml. of glacial acetic acid or 0·5 ml. of 2*N* sulphuric acid, and heat the solution nearly to the boiling point. Then introduce 10 to 12 ml. of the nitron reagent (1), stir, and cool in ice-water for 2 hours. Filter through a weighed filter crucible (Gooch, sintered glass or porous porcelain). Wash with 20 to 40 ml. of a cold saturated solution of nitron nitrate, added in several portions, and drain the precipitate well after each washing. Finally, wash twice with 3 ml. portions of ice cold water. Dry at 105°C (1 hour is usually required), and weigh as $C_{20}H_{16}N_4,HNO_3$.

Note. 1. Prepare the reagent by dissolving 5 g. of nitron in 50 ml. of 5 per cent acetic acid.

IV, 76. CARBONATE

Discussion. The carbonate is decomposed by dilute acid, and either the loss in weight due to the escape of carbon dioxide determined (**indirect method**) or the carbon dioxide evolved is absorbed in a suitable medium and the increase in weight of the absorbent determined (**direct method**). The direct method gives more satisfactory results, and will therefore be described. The indirect method is often employed, however, for samples containing relatively large amounts of carbonate.

The decomposition of the carbonate may be effected with dilute hydrochloric acid, dilute perchloric acid or syrupy phosphoric acid. The last-named acid is perhaps the most convenient because of its comparative non-volatility and the fact that the reaction can be more easily controlled than with the other acids. If dilute hydrochloric acid is employed, a short water-cooled condenser should be inserted between the decomposition flask and the absorption train (see below).

Two absorbents are required, one for water vapour and the other for carbon dioxide. The absorbents for water vapour which are generally employed are : (*a*) anhydrous calcium chloride (14 to 20 mesh), (*b*) magnesium perchlorate trihydrate (" dehydrite "), and (*c*) anhydrous magnesium perchlorate (" anhydrone "). Both (*b*) and (*c*) are preferable to (*a*) ; the former absorbs about 35 per cent and the latter about 50 per cent of its weight of water. They are, however, expensive, and anhydrous calcium chloride is generally employed for ordinary work. The latter usually contains a little free lime, which will absorb carbon dioxide also ; it is essential to saturate the U-tube containing the calcium chloride with dry carbon dioxide for several hours and then to displace the carbon dioxide by a current of pure air.

The absorbents for carbon dioxide in general use are : (*d*) soda lime (this is available also in the form of self-indicating granules, " sofnolite " or as " carbosorb " soda lime, which indicate when the absorbent is exhausted), (*e*) soda lime-asbestos (the " carbosorb " variety gives a marked colour change and therefore indicates the degree of exhaustion), and sodium hydroxide-asbestos (" ascarite "). In all cases the carbon dioxide is absorbed in accordance with the following equation :

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Water is formed in the reaction, hence it is essential to fill one-quarter or one-third of the tube most removed from the carbon dioxide train with any of the desiccants referred to above (Fig. 4-2).

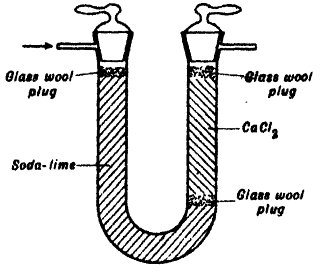

FIG. 4-2.

Determination of carbon dioxide in a carbonate. *Procedure.* Fit up the apparatus shown in Fig. 4-3. **A** is a flask of about 100 ml. capacity, **B** is a dropping funnel containing 20 to 25 ml. of A.R. syrupy phosphoric acid, **C** is a soda-lime guard tube, **D** is a bubbler containing syrupy phosphoric acid, **E** is a U-tube containing calcium chloride which has been saturated with carbon dioxide and the residual carbon dioxide displaced by air (this may be replaced by " dehydrite " or " anhydrone," if available), **F** and **G** are soda lime or " sofnolite " tubes (these may be replaced by " carbosorb " or " ascarite "), and **H** is a guard U-tube containing the same desiccant as in **E.** The U-tubes may be suspended by silver wires attached to hooks on the glass or metal rod **I,** or by some other means. All joints are made with short lengths of stout-walled rubber tubing, and the two ends of the glass tubing should be in contact. Rubber bungs are employed in **A, B** and **C.** Before proceeding with the actual estimation, make sure that the apparatus is gas tight.

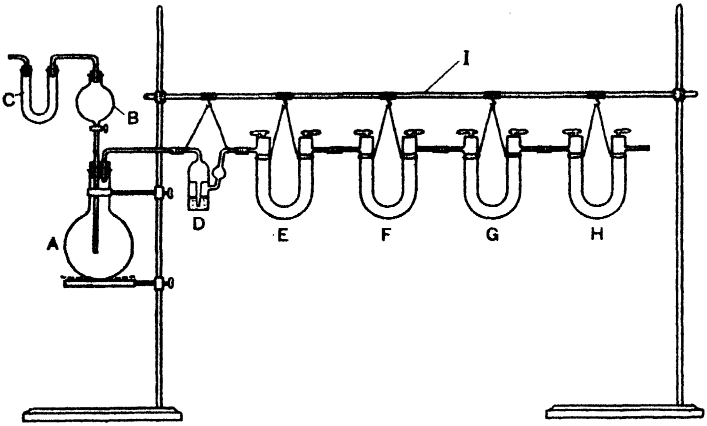

Fig. 4-3.

Weigh out accurately 0·5 to 0·6 g. of the carbonate (1) into the flask **A,** which should be clean and dry. Remove the two soda lime or " sofnolite " tubes **F** and **G,** wipe them with a clean linen handkerchief or cloth, and leave them in the balance case for 45 minutes. Open the taps of the U-tubes momentarily to the air in the balance case, and weigh them separately. Replace them on the drying train ; place 25 ml. of A.R. syrupy phosphoric acid in **B,** and see that the apparatus is connected up as in Fig. 4-3. Open the taps of the U-tubes. Run in sufficient phosphoric acid from the tap funnel to cover the solid in the flask (the 25 ml. will more than suffice). Close the tap of the funnel and heat the flask carefully ; regulate the temperature so that not more than 2 bubbles of gas per second pass through the bubbler **D.** After about 30 to 40 minutes, the contents of the flask should be boiling ; boil for 2 to 3 minutes. Remove the flame, and immediately attach a filter pump and a large bubbler (similar to **D**, and containing syrupy phosphoric acid) to the end of the apparatus. Open the tap funnel, and draw air through the apparatus at the rate of about 2 bubbles per second for 20 minutes. Remove the tubes **F** and **G**, close the taps, treat them as before, and weigh them. From the increase in weight, calculate the percentage of CO_2 in the sample.

Note. 1. For practice in this estimation, the student may employ A.R. calcium carbonate, or any of Ridsdale's " Limestone, Nos. 15, 15b, 15c, or 15d " (Analysed Samples for Students).

IV, 77. Apparatus.—A. Electrolysis unit. The actual set-up employed will vary from one laboratory to another according to the financial resources and the equipment otherwise available. The circuit will, however, be the same in all cases, and this will therefore be considered first. A circuit employing the mains (200 to 240 volts or 110 volts D.C.) is shown in Fig. 4-4; if a D.C. supply is not to hand, some form of rectifier must be employed for A.C. mains. **M** is the D.C. mains, $\mathbf{R_1}$ is a large variable resistance (which may consist of a bank of lamps), $\mathbf{R_2}$ is a smaller variable resistance, **A** is an ammeter reading up to 10 amperes, **V** is a voltmeter reading up to 10 to 15 volts, **E** is the electrolysis vessel, and **S** is a switch. This circuit is perfectly safe; there is no danger of the student receiving any electrical shock in the usual operation at the end of the electrolysis when the electrolyte is replaced by water with the current still flowing. Many types of commercial apparatus, incorporating this circuit, are available.* In general, the two resistances, ammeter and voltmeter are mounted on a board of insulating material, and two terminals are provided for the electrolytic cell. The current may also be supplied by a number of accumulators connected in series; these should possess a sufficiently large ampere-hour capacity

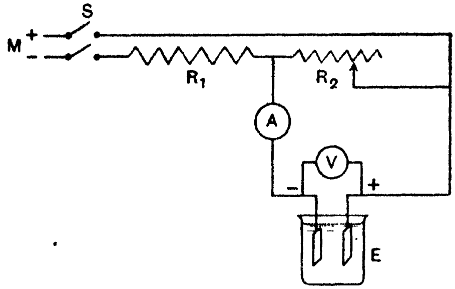

FIG. 4-4.

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* For example, Messrs. A. Gallenkamp and Co. Ltd., of London, England, market two switch-boards for controlling current in electrolyses, one for use with a 10 to 15 volt supply, and the other for operation with a 220 volt D.C. supply mains. The Fisher Scientific Co. of Pennsylvania, U.S.A., supply an "electro-analyser" for use on an 110 volt A.C. circuit; this apparatus is complete with stirrer, stand for electrolysis cell, etc., and can be had in multiple units, thus permitting up to 6 electrolytic determinations to be carried out simultaneously. E. H. Sargent and Co., of Chicago, Ill., U.S.A., manufacture a similar apparatus for use on 110 or 220 volt mains. Attention is also directed to the very useful and comparatively inexpensive Slomin "electrolytic analyser" manufactured by E. H. Sargent and Co. of Chicago. This small apparatus is entirely self-contained, portable, and requires only connexion with the mains (110 volts, 60 cycles A.C. or 220–240 volts 50 cycles A.C.).

to supply a steady current during the whole period of the electrolysis. In the author's laboratory six accumulators of 80 ampere-hours capacity are connected in series, and the electrical connections are such as to permit any electrical pressure up to 12 volts being obtained. These large accumulators are for the low tension supply of the Chemistry Department, and permit of several electro-analyses being conducted simultaneously.

If the polarities of the terminals are not known, they may be determined by touching the two wires from the terminals on to paper moistened with potassium iodide solution ; a brown stain of iodine will form at the positive pole.

A very useful apparatus, and applicable with slight modification to electrolytic, potentiometric and conductimetric analyses, has been designed by H. J. S. Sand* and is shown in Fig. 4-5 ; the circuit is given in Fig. 4-6. The front panel of

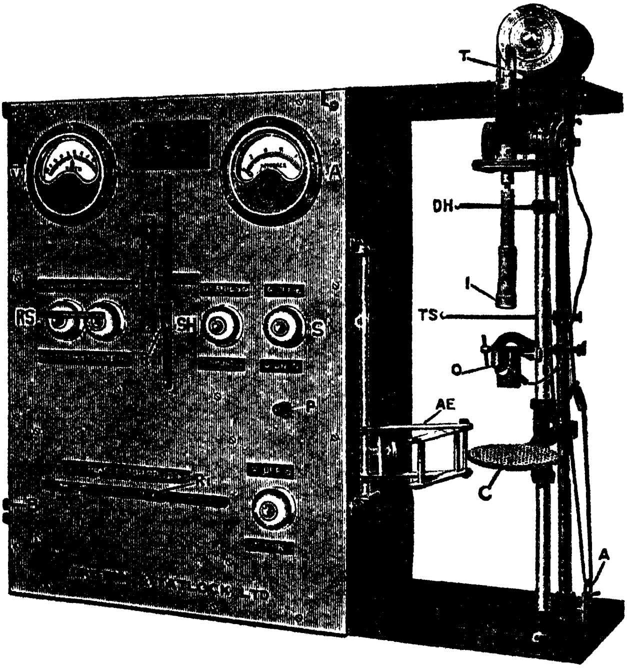


FIG. 4-5.

*** Manufactured by and obtainable from Griffin and Tatlock Ltd., Kemble Street, London, W.C.2, England. The apparatus operates from a 12 or 6 volt supply mains or battery. A car battery may be used ; this can be charged with the ordinary commercial A.C. mains charging set.**

insulating material carries an ammeter **A** (0 to 10 amperes), a voltmeter **V** (0 to 10 volts on either side of the central zero), the main switch **S** for breaking the battery circuit, and a shunt **SH** which allows the rheostat **R** of 15 amperes carrying capacity to be placed in shunt with the battery **B** for separation by graded or controlled potential; the reversing switch **RS** allows the outer electrode to be made either the anode or cathode. At the top of the stand a motor is mounted, which is controlled by a switch and the rheostat $\mathbf{R}_1$. The driving belt passes over two pulleys to a hollow shaft to which a short length of thick-walled rubber tubing **I** is attached. The tubing is closed at the lower end by a stainless steel rod secured to a V-grooved *silver* clutch, and is filled with mercury which allows frictionless electrical contact with the inner electrode to be maintained. The outer (stationary) electrode is supported by a *silver lined* clamp **O**, and the inner (rotating) electrode being provided with a silver or platinum rod at the upper end, is merely pushed into the silver clutch by means of which it is firmly held for the rotation. The ring **C** is a beaker support, and slides on two vertical steel rods, a quick release for it being provided by the ring *A*, which fastens to a hook on the stand. **AE** is an auxiliary electrode holder, for use in supporting the auxiliary electrode required in refined analyses by graded or controlled potential, electrolytic separations, etc.

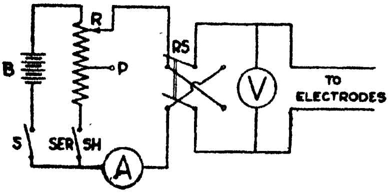
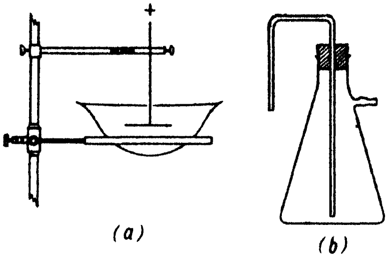


FIG. 4-6.

B. Electrodes. These are generally made of platinum (or platinum-iridium), although cathodes of tantalum are occasionally employed for the deposition of certain metals. Silver electrodes (Fig. 4-10 *a*) are useful as cathodes for copper and zinc determinations. Numerous types of electrodes have been employed. The present tendency is to use gauze electrodes, particularly for the cathode, because they are considered to be the most satisfactory. It is probable that the interstices in the gauze bring about a much better circulation of the electrolyte so far as conditions at the surface of the electrode are concerned, the improved circulation serving to reduce any local depletion of the electrolyte that might tend to occur. It is probable that these gauze electrodes may not be in the possession of every laboratory, so that other, in some cases, less expensive, electrodes will be described also.

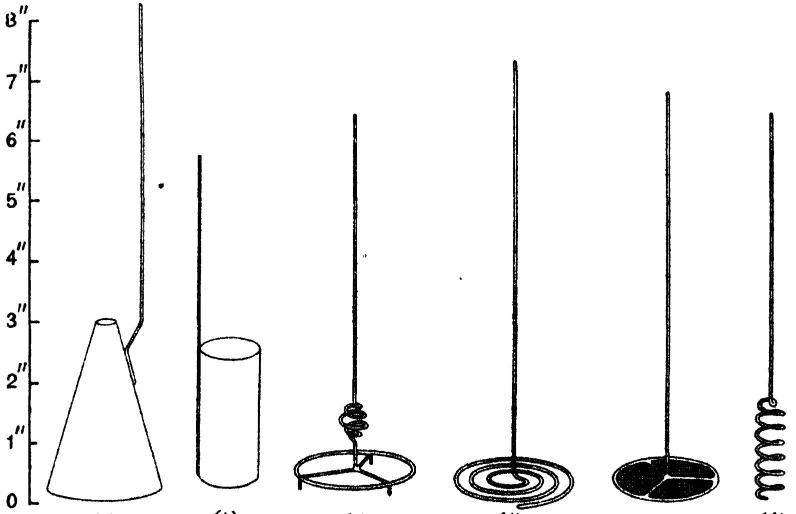
The simplest apparatus is to employ a platinum dish as cathode and a circular platinum plate as anode (Fig. 4-7 *a*): a circular platinum gauze electrode (Fig. 4-8 *e*) may also be used. The filter flask (Fig. 4-7 *b*) is for the removal of the electrolyte after the electrolysis. L. Classen (1927) gives the following details: diameter of dish 9 cm.; depth in the centre 4·2 cm.; capacity about 250 ml.; weight 35 to 40 g.; the inside surface should be matted (*e.g.*, by sand blasting) so that the deposit adheres more easily; surface area for 150 ml. is *ca.* 100 sq. cm., and for 180 ml. of liquid *ca.* 130 sq. cm.; diameter of anode 4·5 cm.; the electrodes should be used exclusively for electrolytic determinations. For a dish 6·5 cm. in diameter, the diameter of the anode should be 3·5 cm.



(*a*) (*b*)

FIG. 4-7.

Two other designs of cathode are shown in Fig. 4-8 *a* and *b*; these are made of platinum sheet and wire. The anodes *c*, *d* and *e* may be used with *a*, and the anode *f* with *b*. These



(*a*) [30 g.] (*b*) [11 g.] (*c*) [25 g.] (*d*) [16 g.] (*e*) [16 g.] (*f*) [16 g.]

FIG. 4-8.

are chiefly employed for stationary or slow electrolysis. The cylinders may be provided with thin slits to facilitate the circulation of the electrolyte. The " flag " type of electrodes are shown in Fig. 4-9 *a* and *b*.

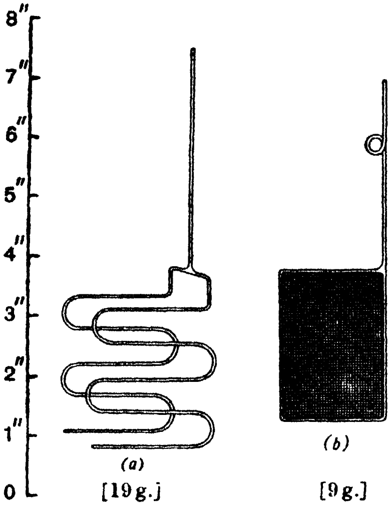


Fig. 4-9.

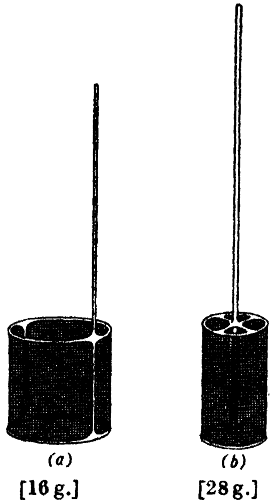


Fig. 4-10.

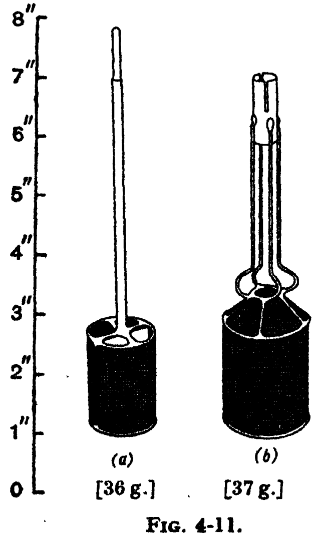
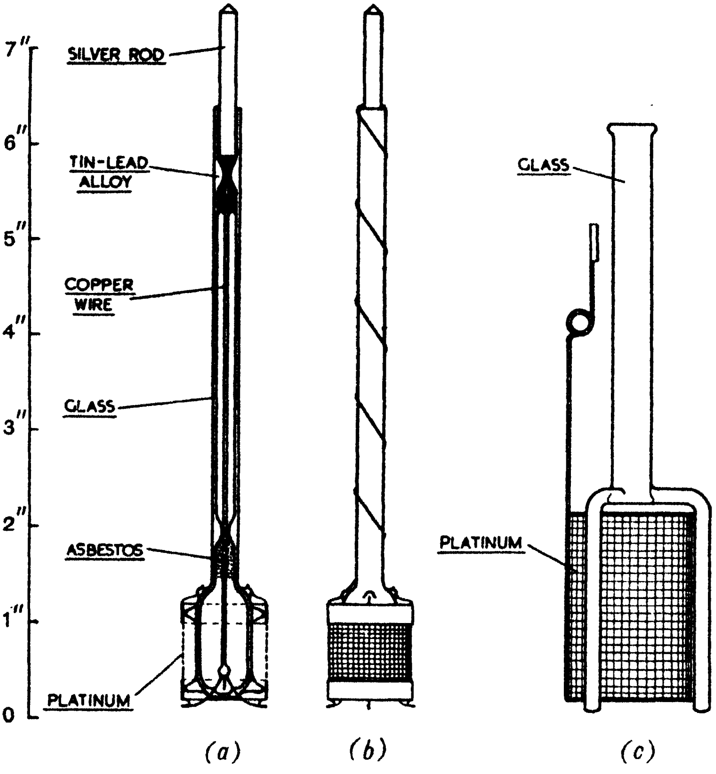


Fig. 4-11.

For routine work in rapid electrolysis a platinum gauze cylinder (Fig. 4-10 *a*) and the associated gauze cylinder (Fig. 4-10 *b*) or spiral (Fig. 4-8 *f*) are generally employed.

Sand's original type (1907) of electrodes for rapid electrolysis are shown diagrammatically in Fig. 4-11 *a* and *b*; a glass sleeve passes through *b* in order to insulate the electrodes from one another. These are particularly well adapted for very rapid electrolysis.

The electrodes shown in Figs. 4-8, 4-9, 4-10 and 4-11 are drawn to one third the actual size, and the approximate weights are indicated.* Sand's original electrodes, although very convenient in use, suffer from the disadvantage that they are expensive. A modification, also due to Sand, which possesses most of the advantages of the original design but requires comparatively little platinum is shown in Fig. 4-12, together with the details of construction.† The inner electrode is made of Pyrex glass,



(a) (b) (c)

[9 g.] [12 g.]

FIG. 4-12.

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* These are reproduced by the courtesy of Messrs. Johnson Matthey and Co. Ltd., of Hatton Garden, London, E.C.1, England. They can of course be modified to suit any particular purpose. Apparatus of smaller dimensions down to " micro " size can be obtained from this firm.

† The author is indebted to Dr. H. J. S. Sand for permitting him to reproduce details of the latest modification of these electrodes. The electrodes are manufactured by Messrs. Griffin and Tatlock Ltd., Kemble Street, London, W.C.2, England. They are drawn half the actual size in the Figure.

and the platinum gauze and the four connecting wires are lightly fused on to the surface of the glass : a platinum wire is wound round the glass to prevent " sticking " during rotation. The outer electrode (*c* in Fig. 4-12) is of platinum gauze and weighs 9 to 12 g. ; it is supported by means of a Pyrex glass tripod, and a terminal is provided for fixing into the silver-lined clamp O of the stand (Fig. 4-5). In use, the stem of the inner electrode is slipped through the guide tube of the tripod and fitted into the holder or clutch (Fig. 4-5 or Fig. 4-16) ; the outer electrode is pushed inside the tripod and both it and the tripod are held by the cathode clamp.

A **mercury cathode** is sometimes employed for special operations. The most important of these is the separation of aluminium from such metals as iron, manganese, chromium, nickel, cobalt, zinc, molybdenum, cadmium, copper, tin, bismuth and lead, which can, under suitable conditions, be deposited on the mercury. The method is therefore of particular value for the *determination of aluminium in steels and alloys.* Three types of mercury cell are shown in Fig. 4-13. In (*a*) the platinum wire is sealed into the side of a lipped Pyrex beaker (250 ml.), whilst in (*b*) the platinum wire is sealed into the side tube, thus permitting the almost complete separation of the aqueous and mercury layers. The platinum terminal is, of course, covered with mercury. Apparatus (*c*) (A. D. Melaven, 1930) is perhaps the most useful form ; the diagram is almost self-explanatory. The electrolysis vessel contains the platinum anode (preferably of the rotating type) immersed in the electrolyte. Electrical contact to the mercury in the levelling bulb is made through a platinum wire

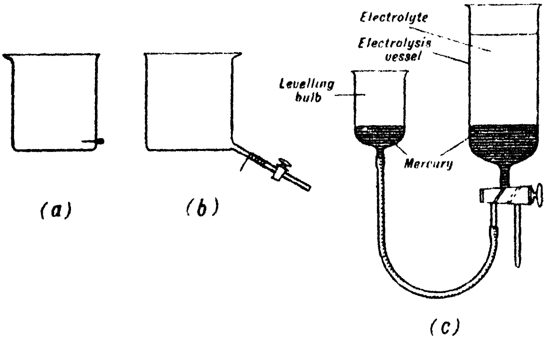

FIG. 4-13.

sealed into its side (alternatively, a pice of copper wire may dip into the mercury) ; the mercury acts as cathode. When electrolysis is complete the levelling bulb is lowered until the mercury reaches the upper end of the stopcock bore ; the stopcock is then turned through 180 degrees and the electrolyte is collected in a suitable vessel. It must be pointed out that in addition to aluminium the following elements are also not removed by electrolysis in a mercury cathode cell : titanium, vanadium, uranium, phosphorus, the alkaline earths and the rare earths ; the anolyte should be sulphuric acid of about $0{\cdot}1N$ concentration.

It is frequently necessary to calculate the current density. For a smooth platinum surface, the estimation of the surface area presents no particular difficulty. As a rough approximation the usual gauze electrode may be regarded as having an effective area twice that of a plain foil electrode of the same dimensions : this applies only if the surface of the foil cathode next to the anode is effective in the deposition. For a closer approximation of the effective area of a gauze electrode, it is probably best to compute the surface area of the wire used in making the gauze. The total length of wire can be calculated from the number of meshes and the dimensions of the electrode. The effective area will then be the total length of the wire multiplied by πd, where d is the diameter of the wire.

C. Electrode vessel. Tall-form beakers, without lip, are generally employed to hold the solution to be electrolysed. These should be of such size that there is the smallest practicable volume of liquid between the cathode and the glass. The apparatus should be so arranged that the beaker can be easily removed without touching any other part of the apparatus, and also so that the electrolyte can be warmed, if necessary. To prevent loss by spraying, split clock glasses with a central hole (Fig. 4-14) are used for covering the electrolytic vessel.

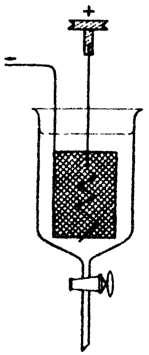

FIG. 4-15.

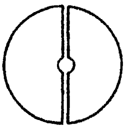

FIG. 4-14.

A form of electrode vessel, which has been employed for rapid electrolysis, is shown in Fig. 4-15. At the end of the electrolysis the solution may be easily drawn off (and used in other determinations, if desired) and the electrodes washed without interrupting the circuit. The disadvantages are: (i) the vessel cannot be heated easily, and (ii) the liquid just above the tap does not readily mix with the bulk of the solution.

D. Stirring. It has already been pointed out (Section **I, 70**) that stirring of the electrolyte during electrolysis reduces considerably the time required for deposition. The method commonly employed is to rotate the inner electrode; this is usually made the anode except in lead determinations (as PbO_2) when it is the cathode. Speeds up to 500 to 1000 revolutions per minute are permissible; those usually employed are 300 to 600 r.p.m. The rotation is generally obtained by drive from an electric motor; a device is always incorporated for varying the speed, for example, an electrical resistance with a D.C. motor, pulleys, gears, etc. Sometimes an independent stirrer is employed, but this is not quite so satisfactory as rotating one of the electrodes.

Many of the commercial apparatus (see Footnote in **A**) have the stirring arrangement incorporated in the main stand. A simple apparatus, utilising Sand's electrodes is shown in Fig. 4-16. The inner electrode is attached through a silver or silver-plated chuck and rubber tubing to a pulley shaft so that it can be rotated; electrical connexion is made through mercury contained in the rubber tube. The cathode is separated from the anode by a glass tube surrounding the stem of the latter, and electrical circuit is completed through the silver-plated clamp holding the stem of the cathode.

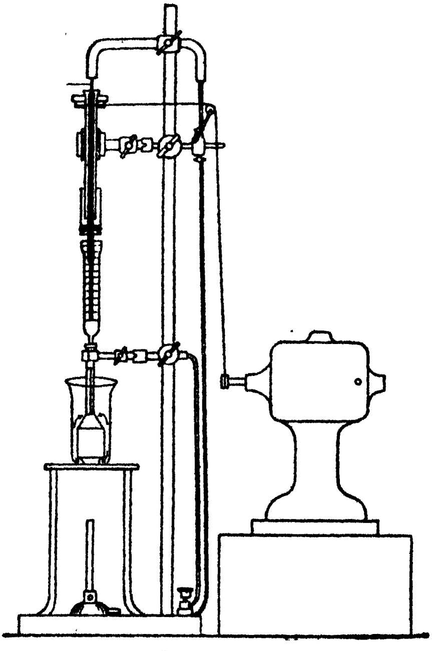

Fig. 4-16.

E. Use and care of electrodes. Electrodes must be free from grease, otherwise an adherent deposit may not be obtained. For this reason an electrode should never be touched on the deposition surface with the fingers ; it should always be handled by the platinum rod or wire attached to the main body of the electrode. Platinum electrodes are easily rendered grease free by heating them to redness in a flame.

Before use electrodes must be carefully cleaned to remove any previous deposits. Deposits of copper, silver, cadmium, mercury, and many other metals can be removed by immersion in dilute nitric acid (1 : 1), rinsing with water, then boiling with fresh 1 : 1 nitric acid for 5 to 10 minutes, followed by a final washing with water. Copper may also be removed by means of a solution composed of 20 g. of trichloroacetic acid, 100 ml. of concentrated ammonia solution and 100 ml. of water. Deposits of lead dioxide are best removed by means of 1 : 1 nitric acid containing a little hydrogen peroxide to reduce the lead to the bivalent form ; alcohol or oxalic acid may replace the hydrogen peroxide. In all cases it is recommended that the electrodes be heated to bright redness over the colourless flame of a Bunsen or Méker type burner before use.

When the electrolysis is complete, the electrode with its deposit is washed by a stream of water (*ca.* 100 ml.) from a wash bottle or other supply while in place and with the current *still on* ; this is necessary since otherwise the electrolyte in contact with the electrode may dissolve some of the deposit. The electrode is then disconnected and rinsed with alcohol* or, better, with pure (*e.g.*, A.R.) acetone (15 to 20 ml.), and then dried at 100° to 110°C for 5 to 10 minutes. In some instances the electrode may be dried by suspending it from a hook clamped to the electrolysis apparatus, and waving a flame below it. The drying should not be prolonged as there may be some danger of oxidising the metal deposit (*e.g.*, with copper). The electrode with its deposit is weighed after cooling to the laboratory temperature. In a few cases, there is evidence that a small transfer of platinum takes place. If this is suspected, the electrode plus deposit should be weighed, the deposit dissolved, the electrode weighed again and the difference taken. The occurrence of anode corrosion is most simply detected by weighing the anode before and after electrolysis.

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* The use of ether after the alcohol washing is not recommended, since ether frequently contains peroxides which may oxidise the metal. If suitable precautions are taken to remove and to prevent the accumulation of peroxides, e.g., by first shaking the ether with potassium permanganate solution or with a weakly acid solution of ferrous sulphate followed by a little water, and then storing in a dark place and including a copper spiral below the cork, ether may be used.

The method adopted for the removal of the electrolyte after the electrolysis is complete will naturally depend upon the type of cell that is employed. With a platinum dish or beaker, the electrolyte may be separated by means of the siphon arrangement shown in Fig. 4-7 *b*, or by some equivalent device. If the electrolysed solution is not to be preserved for a subsequent determination, a very satisfactory method of washing consists in siphoning the solution out of the electrolysis vessel while maintaining the liquid level in the vessel by adding distilled water ; the removal of the electrolyte is shown by the ammeter needle dropping back towards zero. If the beaker rests on a block of wood, the latter may be displaced and the beaker lowered. In the commercial types of apparatus referred to in **A**, a simple device for lowering the beaker is usually incorporated. If the vessel is of the type shown in Fig. 4-15, the liquid is simply run out by opening the tap, and the electrode washed.

Electrolysis must never be carried out in acid chloride solutions since in such solutions corrosion of the platinum occurs, leading not only to erroneous results (the dissolved platinum is plated out on the cathode) but also to injury of the anode.* A number of metals (for example, zinc and bismuth) should not be deposited on a pure platinum surface. These metals, particularly zinc, appear to react with the platinum in some way, for when they are dissolved off with nitric acid the platinum surface is dulled or blackened. Injury to the platinum can be prevented in this case by first plating it with copper, and then depositing the metal on this surface ; alternatively, a silver gauze electrode (as Fig. 4-10 *a*) may be used.

IV, 78. COPPER

Discussion. The general principles of electro-analysis have been discussed in Sections **I, 64** to **I, 70** ; these should be mastered before any determinations are made. Copper may be deposited from either sulphuric or nitric acid solution, but, usually, a mixture of the two acids is employed. If such a solution is electrolysed with an e.m.f. of 2 to 3 volts, the following reactions occur :

Cathode: $Cu^{++} + 2\epsilon \rightleftharpoons Cu$;

$2H^{+} + 2\epsilon \rightleftharpoons H_2$.

Anode: $2OH^{-} \rightarrow 1/2O_2 + H_2O + 2\epsilon$.

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* It has been stated that electrolyses in acid chloride solutions may be carried out in the presence of toluene ; the chlorine liberated during electrolysis is said to react preferentially with the toluene and therefore does not attack the platinum electrodes.

The acid concentration of the solution must not be too great, otherwise the deposition of the copper may be incomplete or the deposit will not adhere satisfactorily to the cathode. The beneficial effect of the nitrate ion is due to its depolarising action at the cathode :

$$NO_3^- + 10H^+ + 8\epsilon = NH_4^+ + 3H_2O.$$

The reduction potential of the nitrate ion is lower than the discharge potential of the hydrogen, and therefore hydrogen is not liberated in the free state. The nitric acid must be free from nitrous acid as the nitrite ion hinders complete deposition and introduces other complications. The nitrous acid may be removed by boiling the nitric acid before adding it, or by the addition of urea to the solution :

$$2HNO_2 + CO(NH_2)_2 = 4N_2 + CO_2 + 3H_2O.$$

The error due to nitrous acid is increased by the presence of a large amount of iron ; iron is reduced by the current to the ferrous state, whereupon the nitric acid is reduced. This error may be minimised by the proper regulation of the *p*H and by the addition of ammonium nitrate instead of nitric acid, or, best, by the removal of the iron prior to the electrolysis.

The solution should be free from the following, which either interfere or lead to an unsatisfactory deposit : silver, mercury, bismuth, selenium, tellurium, arsenic, antimony, tin, molybdenum, gold and the platinum metals, thiocyanate, chloride, oxidising agents such as oxides of nitrogen, or excessive amounts of ferric nitrate or nitric acid. The electrolytic deposit should be salmon-pink in colour, silky in texture, and adherent. If it is dark, the presence of foreign elements and/or oxidation is indicated. Spongy or coarsely crystalline deposits are likely to yield to high results ; they arise from the use of too high current densities, or improper acidity and absence of nitrate ion.

Procedure. The solution (100 ml.) may contain 0·2 to 0·3 g. of Cu (1). Add cautiously 2 ml. of concentrated sulphuric acid, 1 to 1·5 ml. of concentrated nitric acid (the latter should be freshly boiled in order to remove oxides of nitrogen), and transfer to, unless already present in, the electrolysis vessel. For simplicity of description, it will be assumed that the cathode is of the gauze form (Fig. 4-10 *a*) and the anode is either a thick platinum wire spiral (Fig. 4-8 *f*) or a gauze cylinder (Fig. 4-10 *b*) ; the student should be able to readily adapt the procedure to other types of electrode if he reads Section **IV, 77** carefully. Clean the platinum gauze cathode by heating it in 1 : 1 nitric acid, and washing it thoroughly with distilled water. Dry the electrode at 100° to 110°C, cool in a desiccator, and weigh. Handle the electrode by the stem and not by the gauze, since a trace of grease may cause a non-adherent deposit of copper. Arrange the circuit as shown in Fig. 4-4, or suitably adapted according to the source of current (if accumulators or storage batteries supplying not more than 12 volts are employed, one large resistance will suffice), but do not connect the source of current (2). Be sure that the cathode is connected to the negative terminal and the anode to the positive terminal. If a rotating anode is to be used subsequently, make certain that it can rotate without coming into contact with the cathode at any point. Place the electrolysis vessel in position (*e.g.*, a beaker resting on a wooden block or upon a stand), and adjust the height so that the electrodes extend nearly to the bottom of the beaker and the cathode is 80 to 90 per cent immersed in the solution. Cover the electrolysis vessel (beaker) with a split clock glass (Fig. 4-14), and with all the resistance in the circuit, so that only a small current will flow, close the circuit and proceed as (**A**) or (**B**), depending upon whether or not stirring is employed.

(**A**). **Slow electrolysis, without stirring.** With an applied potential of 2 to 2·5 volts, adjust the resistance until a current of approximately 0·5 amp. flows, as indicated by the ammeter in the circuit ; electrolyse, preferably overnight (3). Rinse off the split clock glasses and test for complete deposition after the blue colour of the solution has disappeared. This is best done by adding more water to raise the level of the electrolyte (say, by 0·5 cm.) and continuing the electrolysis for 30 minutes. If at the end of this time no copper deposit has appeared on the freshly immersed surface of the cathode, it may be assumed that the deposition is complete. If a deposit does form, continue the passage of the current as long as may be judged necessary, and again test as before. If the solution is not to be used for a further estimation, a drop or two of it may be removed and tested with sodium acetate and hydrogen sulphide water or with potassium ferrocyanide solution.

(**B**) **Rapid electrolysis, with stirring.** Start the motor driving the anode (or, less satisfactorily, the glass propeller) and adjust its speed (300 to 800 r.p.m.) so that the solution is vigorously stirred without there being any danger of mechanical loss of liquid. Use a voltage across the terminals of the cell of 3 to 4 volts, and adjust the resistance so that the current is 2 to 4 amps. Continue the electrolysis until the blue colour of the solution has entirely disappeared (usually somewhat less than 1 hour), reduce the current to 0·5 to 1 amp., and test for completeness of deposition by rinsing the split clock glasses, raising the level of the liquid by about 0·5 cm. by the addition of distilled water, and continuing the electrolysis for 15 to 20 minutes. If no copper plates out on the fresh surface of the cathode, electrolysis may be regarded as complete.

When electrolysis has been shown to be complete, the subsequent procedure is the same whether slow or rapid electrolysis has been employed. Two methods may be employed : (i) is used only when the residual electrolyte is not required for further determination, and (ii) is of universal application.

(i) Siphon off the liquid (for example, with a glass siphon provided with a stop cock). Whilst siphoning the heavier liquid from the bottom of the beaker, add water from the top to keep the level of the liquid in the electrolysis vessel nearly constant. Continue this process until the ammeter needle drops practically to zero. Then rinse the cathode with a little pure alcohol or with A.R. acetone (4), and dry it for 5 to 10 minutes at 100° to 110°C. Weigh when cold.

(ii) Lower the beaker very slowly, or raise the electrodes, and at the same time direct a continuous stream of distilled water from a wash bottle or supply bottle against the upper edge of the cathode. This washing must be done immediately the cathode is removed out of the solution and the circuit must not be broken during the process. When the cathode has been thoroughly washed, break the circuit, dip the cathode into a beaker of distilled water, and then rinse it with alcohol or A.R. acetone (4). Dry at 100° to 110°C for 5 to 10 minutes, and weigh when cold.

From the increase in weight of the cathode, calculate the copper content of the solution. After the cathode has been weighed, it should be cleaned with nitric acid as described in Section **IV, 77,** and reweighed ; the loss in weight will serve as a check.

Notes. 1. Larger quantities of copper may be present, particularly if rapid electrolysis is employed ; the quantity given is, however, convenient for instructional purposes. For practice in the determination, the student may prepare the solution *either* by weighing out accurately about 1 g. of A.R. copper sulphate pentahydrate *or* by dissolving about 0·25 g., accurately weighed, of A.R. copper in 1 : 1 nitric acid, boiling to remove nitrous fumes, just neutralising with ammonia solution, and then just acidifying with dilute sulphuric acid and diluting to 100 ml.

2. This is, of course, unnecessary if a commercial " electro-analyser " or electrolysis unit is employed.

3. If conditions do not allow this practice, use a current of 1·5 to 3·0 amps. : deposition is usually complete in 2 to 4 hours. This procedure is, however, less satisfactory.

4. This is best effected by completely immersing the cathode in a beaker containing pure alcohol or acetone.

IV, 79. LEAD

Discussion. Lead is deposited quantitatively as the dioxide at the anode in the presence of a high concentration of nitric acid (15 ml. of concentrated acid per 100 ml. of the electrolyte). With a gauze anode of the usual size (Fig. 4-10 *a*) about 0·1 g. of lead is the maximum that can be firmly deposited. With a platinum dish (matted or sand blasted internal surface) as anode, quantities up to 2 g. may be readily deposited ; this method is therefore frequently employed when large quantities of lead are to be determined in one operation.

It is difficult to remove all the water from the electrode by drying at low temperatures. For a temperature of 120°C, the conversion factor 0·8640 instead of the theoretical conversion factor of 0·8662 is employed. However, by drying at 220°C for about an hour, the theoretical factor may be employed for quantities up to 0·1 g. For quantities of 0·1 to 0·3 g., the factor 0·8650 has been recommended, whilst for larger weights 0·8635 has been suggested (L. Classen, 1927). A useful method is to dissolve the dioxide, without drying, in standard oxalic acid solution, and to titrate the excess with standard potassium permanganate solution.

The following interfere in this determination : mercury, arsenic, antimony, tin, selenium, tellurium, phosphorus, chromium, chloride, iodide, silver, bismuth and manganese (the last three metals tend to form peroxides at the anode).

Procedure. For a platinum gauze electrode (Fig. 4-10 *a*), the solution (100 ml.) should contain not more than 0·1 g. of Pb as lead nitrate, 15 ml. of concentrated nitric acid, and none of the interfering elements mentioned above. Somewhat greater quantities may be deposited with the aid of Sand's electrodes (Figs. 4-11 and 4-12). Larger quantities of lead are generally determined, as already pointed out, with a platinum (Classen) dish. The present details apply, however, chiefly to the gauze electrode, but can be readily adapted to the use of a platinum dish.

Heat the anode to 220°C in an electric oven for 1 hour, allow to cool in a desiccator, and weigh. Connect up the cell with the positive terminal of the source of current on to the gauze anode or platinum dish, and the negative terminal to the wire or gauze cathode (1). Adjust the current to 0·05 to 0·1 amp. at 2 volts with the aid of the rheostat, and allow the electrolysis to proceed overnight. Test for completeness of deposition by adding about 20 ml. of distilled water and continuing the electrolysis for 15 minutes ; if no darkening of the freshly-covered anode surface occurs, deposition is complete. When the electrolysis is complete, either lower the beaker from the electrodes or slowly raise the electrodes out of the solution without interrupting the current, and at the same time rinse the electrodes very thoroughly with a jet of water from a wash bottle or from a storage bottle. Then disconnect the source of current, wash the anode with alcohol or acetone, and dry at 220°C ; cool in a desiccator and weigh.

The determination may be carried out more rapidly by one of the following methods. In these the outer electrode is the anode.

(i) With a current of 1·5 to 2·0 amps. at 2 volts at the ordinary temperature. Electrolysis is complete in about 1·5 hours.

(ii) With a current of about 1·5 amps. at 2 volts at 50° to 65°C. About 0·1 g. of lead dioxide can be deposited in 12 to 18 minutes ; the solution should contain 20 per cent of its volume of concentrated nitric acid.

(iii) With 2 volts and an initial current of 0·5 amp., which is subsequently raised to 5 amps. 0·1 Gram of lead dioxide may be deposited in 6 to 8 minutes at room temperature : this time is still further reduced by working at about 60°C.

The deposited dioxide is removed from the electrode, after weighing as above, by immersion in warm 1 : 1 nitric acid to which a little pure hydrogen peroxide has been added. As an additional check the solution may be evaporated with sulphuric acid, and the lead determined as sulphate (Section **IV, 14A**).

Note 1. Full experimental details of the general technique are given under Copper (Section **IV, 78**), and will therefore not be repeated in the description of this and succeeding determination.

IV, 80. CADMIUM

Discussion. Cadmium is best determined from a faintly alkaline solution containing only enough potassium cyanide to keep the cadmium in solution, *i.e.*, containing the complex $K_2[Cd(CN)_4]$ (*Procedure A*). Less accurate results, but sufficiently precise for most routine analyses, may be obtained in very dilute sulphuric acid solution ; higher current densities are permissible when a rotating electrode is employed (*Procedure B*).

Procedure A. The solution should contain about 0·4 g. of Cd as the sulphate, acetate, or, less desirably, the nitrate. Add a drop of phenolphthalein, followed by *ca.* 0·1*N* sodium or potassium hydroxide until a permanent pink colour is just obtained. Then add a solution of pure (*e.g.*, A.R.) potassium or sodium cyanide dropwise and with constant stirring until the precipitated cadmium hydroxide just dissolves. A large excess of alkali cyanide should be avoided. Dilute to 100 to 150 ml., and electrolyse the cold solution, preferably with a weighed platinum gauze cathode, and a current of 0·5 to 0·7 amp. at 4·8 to 5·0 volts (1). At the end of 6 hours, increase the current to 1·0 to 1·2 amps., and continue the electrolysis for another hour. Wash the split clock glass and the sides of the beaker with about 20 ml. of water, and continue the electrolysis for 15 minutes. If the newly exposed surface of the cathode remains bright, thus indicating that the deposition of the cadmium is complete (2), remove the electrolyte from the electrodes, rinse immediately with water, stop the current, and rinse the cathode with alcohol or A.R. acetone. Dry at 100°C, cool, and weigh. Test the residual electrolyte for cadmium by any of the recognised tests.

The determination may be carried out more rapidly by using a rotating cathode (600 to 800 r.p.m.) with a current of 1·5 to 2·0 amps. at 2·7 to 3·0 volts. 0·2 Gram of Cd may thus be deposited in 30 minutes.

Procedure B. The cadmium should be present in the solution (100 ml.) as sulphate ; nitrates and chlorides must be absent. The maximum concentration of free sulphuric acid is 0·5N, and 5 g. of potassium hydrogen sulphate is added. Electrolyse at room temperature with 0·1 to 0·2 amp. at 2·4 to 2·8 volts ; after 3 hours, increase to 0·5 amp. until electrolysis is complete. 0·3 Gram of Cd is thus deposited in 3 to 4 hours.

Alternatively, use a rotating electrode with 1·5 to 0·7 amps. at 2·7 volts. 0·2 Gram of Cd may thus be deposited in 20 minutes.

Notes. 1. If left overnight, use a current of 0·2 to 0·3 amp. at 2·8 to 3·2 volts.

2. It is sometimes difficult to detect the deposition of the bright cadmium on the platinum surface. This difficulty is readily overcome by heavily plating the platinum electrode with copper or silver first, and then proceeding with the electrolysis in the usual manner. An added advantage is that the removal of the cadmium after the electrolysis is rendered more facile; also, if the temperature of drying should accidentally exceed 100°C, there is little danger of harming the platinum electrode.

IV, 81. NICKEL

Discussion. The most satisfactory method for the determination of nickel by electrolysis is from strongly ammoniacal solution containing ammonium sulphate. The nickel is present largely as the complex ion :

$$[Ni(NH_3)_6]^{++} \rightleftharpoons Ni^{++} + 6NH_3,$$

and is deposited as a dense adherent layer, bright silver-grey in colour, upon the cathode. The nickel should be present preferably as the sulphate, but the chloride may also be employed ; the nitrate introduces difficulties, and should be absent. The metals of the hydrogen sulphide group, zinc, vanadium, tungsten, molybdenum, chromates and ferrous salts should be absent ; cobalt is deposited with the nickel. *Small* amounts of the precipitated hydroxides, such as that of iron, are not occluded by the deposit to any appreciable extent ; as a general rule, however, they are best removed first. The electrolysis should not be unduly prolonged, because there is a slight tendency towards solution of the anode, with subsequent deposition of platinum upon the cathode.

Procedure. The solution should contain not more than about 0·2 g. of Ni as sulphate or chloride. Add 5 to 10 g. of ammonium sulphate, 30 to 40 ml. of concentrated ammonia solution, and dilute to 150 ml. Electrolyse using 1 amp. at 3 to 4 volts ; about 0·15 g. of Ni is deposited in 2 hours (1). Test for completeness of precipitation in the usual way by adding about 20 ml. of water, and continuing the electrolysis for 15 to 20 minutes ; no nickel should be deposited on the freshly immersed surface (2). Alternatively, the dimethylglyoxime test, suitably modified, may be applied. Wash, dry and weigh the cathode as in the estimation of Copper (Section **IV, 78**).

The determination may be carried out more rapidly by using a rotating electrode with 4 amps. at 3-4 volts. 0·1 Gram of nickel is thus deposited in about 10 minutes.

The nickel is best removed from the electrode by means of dilute mineral acids ; concentrated nitric acid should not be employed because of the danger of inducing passivity.

Note. 1. With a current of 0·2 to 0·3 ampere, the deposition is generally complete in 12 to 15 hours. This current is used if the electrolysis can be allowed to proceed overnight.

2. This test is not always satisfactory, for deposits of nickel are sometimes obtained which can hardly be distinguished from the platinum of the electrode (compare Cadmium, Section **IV, 80,** Note 2).

IV, 82. COBALT

Discussion. The determination of cobalt follows along the same lines as given under Nickel (Section **IV, 81**). The addition of a little hydrazine sulphate improves the character of the cathode plate by reducing the tendency to form an oxide deposit at the anode.

IV, 83. SILVER

Discussion. Silver may be determined by electrolysis in nitric, ammoniacal or cyanide solutions. In cyanide solution the silver is present largely as the complex ion :

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^- ;$$

an excellent plate is obtained, and separation from other elements (*e.g.*, copper and lead) may be effected. The cyanide method will be described.

The disadvantage of the electrolytic method is that so many other elements are also deposited, either wholly or in part, that a number of preliminary separations are usually required before it can be applied. For this reason, it is not widely employed.

Procedure. The silver (*ca.* 0·2 g.) should be present in solution as the nitrate. Add pure (*e.g.*, A.R.) potassium cyanide until the precipitate of silver cyanide is dissolved, and then add an excess such that about 3 g. of potassium cyanide is present in the solution. Dilute to 100 to 120 ml. Electrolyse with 0·2 to 0·5 amp. at 3·7 to 4·8 volts at 20° to 30°C ; about 0·1 g. of Ag is deposited in 3 hours. Alternatively, electrolyse with a rotating electrode with 1 to 0·5 amp. at 2·5 to 3·2 volts ; 0·2 g. of Ag is deposited in 20 to 25 minutes. Completeness of deposition is tested for by transferring a few drops of the electrolyte to a test tube, acidifying with a little nitric acid, boiling off the hydrocyanic acid (*caution* : *poisonous*), rendering ammoniacal, and adding a few drops of ammonium sulphide solution ; no brown precipitate should be obtained. The determination is completed as under Copper (Section **IV, 78**).

Note. If insoluble silver salts are to be analysed, *e.g.*, chloride, bromide, iodide and oxalate, these may be dissolved directly in the potassium cyanide solution.

IV, 84. ZINC

Discussion. Zinc is quantitatively deposited from an alkaline zincate solution containing excess of alkali. The proportion of alkali is not of great importance provided that it exceeds a minimum of 10 molecules of alkali hydroxide to 1 molecule of zinc salt : it is unnecessary to employ a larger excess of alkali than is required to keep the solution clear during the whole of the electrolysis. Ammonium salts, if present, must be decomposed by the addition of excess of caustic alkali and boiling. Chlorides and nitrates interfere ; they must be removed, if present, by evaporation to fuming with sulphuric acid.

Zinc should not be directly deposited on a platinum surface as it is difficult to remove it completely (it tends to leave black stains) and upon heating may alloy with the noble metal. The platinum electrode should be plated with copper or, preferably, with silver. Alternatively, a silver gauze cathode (as Fig. 4-10 *a*) may be used. Cathodes of nickel have also been used, and are quite satisfactory.

A useful application of the electrolytic method is in the analysis of alloys containing aluminium and zinc.

Procedure. For practice in this method, weigh out accurately about 0·3 g. of A.R. zinc oxide, dissolve it in the minimum volume of dilute sulphuric acid, add a solution of 7 g. of A.R. sodium hydroxide in water, stir until the solution is clear, dilute to 125 ml., and electrolyse using a copper or silver plated platinum cathode or a silver cathode. For slow electrolysis, use a current of 0·4 to 0·8 amp. at 3·8 to 4·2 volts. For rapid electrolysis (rotating electrode), the current may be increased up to 5 amps. The metal is more rapidly deposited at about 60°C. When electrolysis is complete, remove the solution without interrupting the current, wash thoroughly with water, then with alcohol or acetone, dry at 60° to 70°C, and weigh. Calculate the percentage of Zn in the sample.

IV, 85. Electrolytic separation and determination of copper and nickel.—

Discussion. This determination has been included at this stage in order to indicate the use of the electrolytic method in the separation and determination of metals. The theory is discussed in Section **I, 69.** There are a number of alloys, which include Monel metal, certain coinage alloys (*e.g.*, American), and " cupro-nickel," which are composed principally of copper and nickel, together with small amounts of iron and manganese and not more than traces of other elements. These are suitable for this exercise in electrolytic separation.

The copper is determined in strongly acid solution at a potential not exceeding 4 volts (above this potential nickel may plate out). The solution is evaporated to fuming in order to remove excess of nitric acid, the iron present is precipitated with ammonia solution, and the nickel deposited from the filtrate after the addition of a large excess of ammonia solution.

The separation of **lead and copper** by electrolysis is described in Section **IV, 87** (analysis of brass).

Silver and copper in silver-copper alloys (silver solder, sterling silver, and certain coinage alloys) may be separated and determined electrolytically by dissolving the sample in 1 : 1 or 1 : 2 nitric acid, removing the excess of nitric acid by evaporation, and then estimating the silver after the addition of excess of pure potassium cyanide at a voltage not exceeding 1·5 (Section **IV, 83**). The residual solution is acidified with nitric acid, the hydrocyanic acid boiled off, and the copper deposited as detailed in Section **IV, 78.** Alternatively, the silver may be deposited from ammoniacal solution (5 ml. of free concentrated ammonia solution per 100 ml. of solution). Most of the silver is deposited with a current of 0·4 amp., a little hydrogen peroxide is added to oxidise cuprous salts and to redissolve any particles of silver not plated on the electrodes, and the deposition completed at 0·2 amp. It is essential that the solution be vigorously stirred during the whole of the estimation. The copper is determined in the residual electrolyte after acidifying with nitric acid and diluting.

Procedure (**analysis of a copper-nickel alloy**). Weigh out accurately about 0·5 g. of the clean alloy (1) into a 150 ml. beaker, which should be suitable as an electrolytic vessel. Add a mixture of 10 ml. of water, 1 ml. of concentrated sulphuric acid and 2 ml. of concentrated nitric acid to dissolve the alloy. When solution is complete, boil off the oxides of nitrogen, and dilute to 100 ml. The solution is now ready for the deposition of copper.

Copper. Proceed as directed in Section **IV, 78,** and employ either the slow or rapid method of electrolysis. Wash the copper deposit thoroughly with water, and keep the solution for the estimation of iron and nickel.

Iron. Evaporate the solution and washings from which the copper has been removed on a low temperature hot plate as far as possible, and then heat at a higher temperature until fumes of sulphur trioxide appear. Cool the residue, and carefully add water until the volume is about 25 ml. Precipitate the small quantity of iron that is now present in the ferric state by adding to the warm solution about 10 ml. of 1 : 1 ammonia solution in excess. Filter through a small quantitative filter paper, and collect the filtrate in a 150 ml. electrolytic beaker (*A*). Wash the precipitate three times with water. Place the original beaker under the filter; dissolve the precipitate in a little hot 1 : 5 sulphuric acid and wash the paper with water. Precipitate the iron again with the same large excess of 1 : 1 ammonia solution, and filter through the same paper. Wash the precipitate, and collect the filtrate and washings in beaker (*A*) containing the filtrate and washings from the first precipitation. Ignite the ferric hydroxide to ferric oxide, and weigh it (Section **IV, 8**).

Nickel. Add 15 ml. of concentrated ammonia solution to the ammoniacal nickel solution, and dilute to 100 to 120 ml. Carry out the determination as detailed in Section **IV, 81.**

Calculate the percentage of copper, iron and nickel in the alloy.

Note. 1. Either Ridsdale's "Cupro-Nickel, No. 19" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Cupro-Nickel 'A'" (one of the British Chemical standards) is suitable for this estimation.

IV, 86. SIMPLE GRAVIMETRIC SEPARATIONS

Discussion. The author has found it a good practice in his own classes for students to undertake simple gravimetric separations before embarking upon the analysis of complex materials. This scheme may not commend itself to all teachers, chiefly on the ground that the mixtures are artificial and are therefore not likely to be encountered as such in practice; however, the analysis of simple artificial mixtures is a valuable preliminary training before proceeding to the analysis of complex materials.

Many separations have been briefly indicated in the text; a few are given in detail. With his knowledge of the determination of the component elements, the student should experience no difficulty in carrying out the undermentioned separations and estimations.

Procedure. **A. Iron and aluminium.** *Method 1.* Dissolve the mixture provided (1) in water or in dilute hydrochloric acid in a Pyrex beaker, and dilute to 75 ml. (2). Heat to about 70°C, and add an excess (8 to 10-fold) of 0·2*N* sodium hydroxide (A.R.) slowly and with constant stirring (3). The excess of alkali will dissolve the precipitated aluminium hydroxide as sodium aluminate. Dilute to 150 ml. with boiling water, boil for several minutes, and filter. Wash the beaker, precipitate and filter with hot water until the washings are at most faintly alkaline. Reserve the filtrate and washings (i). Place the original beaker under the filter, dissolve the precipitated ferric hydroxide by pouring warm 2*N* hydrochloric acid upon it (4), and then reprecipitate the iron with ammonia solution (Section **IV, 8**), or by any of the methods given in Section **IV, 31.** Ignite and weigh as Fe_2O_3.

Determine the aluminium in the filtrate (i) either by acidifying with dilute hydrochloric acid, adding several grams of ammonium chloride, and precipitating with dilute ammonia solution (Section **IV, 9**), or by just acidifying with dilute hydrochloric acid and precipitating with sodium thiosulphate solution (Section **IV, 28A**); in both cases the precipitate is ignited to and weighed as Al_2O_3. Alternatively, the oxine method (Section **IV, 28B**) may be used.

Notes. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. iron alum and A.R. ammonium alum.

2. If ferrous iron is present, oxidise it with a little concentrated nitric acid.

3. Improved results may be obtained by the following method of precipitation. Nearly neutralise the dilute acid solution of iron and aluminium with aqueous sodium hydroxide, heat to boiling, and add the solution slowly and with constant stirring to 75 ml. of hot 5 per cent sodium hydroxide (A.R.) solution. Boil the mixture for 2 to 3 minutes with gentle stirring, and filter.

4. It is difficult to completely free the precipitate from sodium hydroxide, etc.; this is most simply achieved by reprecipitation.

Method 2. This procedure depends upon the precipitation of iron by ammonium sulphide in ammonium tartrate solution : aluminium (also chromium, vanadium, titanium, zirconium and beryllium) is not precipitated under these conditions.

Dissolve the mixture provided in water or in dilute hydrochloric acid in a conical flask, and dilute to 75 to 100 ml. Add 4 times as much pure tartaric acid as the dissolved metals would weigh as oxides, render alkaline with ammonia solution (the solution should remain clear if enough tartrate is present), acidify with 1 : 1 hydrochloric acid, and add 2 ml. in excess. Saturate with hydrogen sulphide to reduce the iron (also to take advantage of the fact that ferrous sulphide is filtered more easily than ferric sulphide). Add a slight excess of dilute ammonia solution, introduce more hydrogen sulphide, and allow the precipitate to settle in the closed flask. Filter off the precipitated ferrous sulphide, wash thoroughly with water containing a little ammonium sulphide and ammonium tartrate, and keep the filtrate and washings (i). Dissolve the precipitate in 1 : 1 hydrochloric acid. Alternatively, place the precipitate and paper in a beaker of suitable size, cover with a clock glass, and cautiously dissolve the sulphide in 1 : 1 hydrochloric acid : heat until all the black particles have disappeared, and shred the paper by vigorous stirring with a policeman. Oxidise the iron by the addition of 1 ml. of concentrated nitric acid, boil, dilute, and precipitate the iron as in *Method 1.* Weigh as Fe_2O_3.

To determine the aluminium, the excess of tartrate must be destroyed. Add cautiously 10 to 12 ml. of concentrated sulphuric acid to the filtrate (i), evaporate in a large platinum dish, and heat carefully until the solution begins to show signs of charring. Allow to cool, cover with a clock glass, and add 5 ml. of concentrated, better of fuming, nitric acid. When the violent action has ceased, heat gradually until the organic matter is fully oxidised ; repeat the treatment with nitric acid, if necessary. Cool, dissolve the residue in water, and precipitate the aluminium with ammonia solution as in Section **IV, 9.** Weigh as Al_2O_3.

Method 3. This method illustrates the use of cupferron in separating iron (and also titanium, zirconium and vanadium) from aluminium (and also from chromium, manganese and nickel). Precipitation is made in strongly acid solution.

Dissolve the mixture provided in water or in dilute sulphuric acid. Dilute to 150 ml., and add cautiously 15 ml. of concentrated sulphuric acid. Cool to 10°C, and then introduce a freshly-prepared, cold 6 per cent aqueous solution of cupferron slowly and with constant stirring until an excess* is present. A reddish-brown flocculent precipitate is produced; precipitation is complete when a white, finely crystalline precipitate of cupferron appears. Add a Whatman accelerator (or one-third of an ashless tablet), allow to settle for 2 to 3 minutes, and filter with gentle suction through a quantitative filter paper supported on a filter cone (Whatman, hardened, No. 52). Wash the precipitate with cold 10 per cent by volume sulphuric or hydrochloric acid, then twice with 5*N* ammonia solution to remove excess of the reagent, and finally once with water. Reserve the filtrate and washings (i). Complete the determination as in Section **IV, 31B.** Weigh as Fe_2O_3.

To estimate the aluminium, concentrate the filtrate and washings (i) to 25 ml., add 20 to 25 ml. of concentrated nitric acid, and evaporate slowly to fumes of sulphuric acid. Treat with more nitric acid if organic matter is still present. Finally, evaporate just to dryness, dissolve the residue in water, and complete the determination as in *Method 2.*

For other methods of separation, see Section **IV, 95, C1** and **C2.**

B. Iron and Chromium. *Method 1.* Dissolve the mixture (1) in water or in dilute hydrochloric acid, almost neutralise with A.R. sodium hydroxide solution, and heat to boiling. Pour this solution slowly and with constant stirring into 100 ml. of a hot, 5 per cent A.R. sodium hydroxide solution, boil for 2 to 3 minutes, and cool to the laboratory temperature. Treat with bromine water until the solution is yellow (alternatively, add a few ml. of 100-volume hydrogen peroxide); boil to decompose the excess of hypobromite (or of hydrogen peroxide). The chromium will now be in solution as chromate. Add a Whatman accelerator (or one-third of an ashless tablet), allow the precipitate to settle, and filter through a quantitative filter paper. Wash the precipitate with hot water, and reserve the filtrate and washings (i). It is advisable to dissolve the precipitate in 2*N* hydrochloric acid, and to reprecipitate the ferric hydroxide as in **A,** *Method 1.* Weigh as Fe_2O_3.

If sulphate is absent, the chromium may be determined as barium chromate. Render the filtrate (i) acid with acetic acid, and add an excess of barium acetate solution. Complete the estimation as in Section **IV, 30C.** Weigh as $BaCrO_4$.

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* About 33 per cent excess, *i.e.*, 0·83 g. of cupferron for 0·1 g. of Fe.

If sulphate is present, acidify the filtrate (i) with hydrochloric acid, reduce the solution by the addition of 15 ml. of alcohol, and boil. Precipitate the chromium as chromic hydroxide as in Section **IV, 9** or Section **IV, 30A.** Weigh as Cr_2O_3.

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. iron alum and A.R. chrome alum.

Method 2. Here the chromium is oxidised in *acid* solution by perchloric acid to chromate (1).

Weigh out a suitable quantity of the mixture into a conical flask, add 5 ml. of water and 5 ml. of A.R. 60 to 70 per cent perchloric acid (**DANGER**; see Section **IV, 70**), and place a short funnel in the mouth of the flask. Heat in the fume cupboard until the solution has evaporated to half its original volume, and has assumed a deep orange colour for at least 5 minutes; oxidation is then complete. Allow to cool, add 40 to 50 ml. of water, and boil for 2 to 3 minutes to drive off any free chlorine which may be present (test with starch-iodide paper). Transfer quantitatively to a 250 ml. beaker, and precipitate the iron by the addition of ammonia solution in the usual manner (Section **IV, 8**). Keep the filtrate and washings (i). The ferric hydroxide should be dissolved in $2N$ hydrochloric acid and reprecipitated. Weigh as Fe_2O_3.

Determine the chromate in the filtrate and washings (i) as in *Method 1* or by the following **volumetric process.** Acidify with 1 : 1 hydrochloric acid, transfer quantitatively to a 350 or 500 ml. glass-stoppered bottle, and treat with 30 ml. of 10 per cent potassium iodide solution and 5 ml. of concentrated hydrochloric acid. Add 50 ml. of water, and allow to stand for 1 minute. Titrate the liberated iodine with standard $0{\cdot}1N$ sodium thiosulphate: add starch solution towards the end, and continue the titration until the green colour appears.

$$1 \text{ Ml. } N\ Na_2S_2O_3 \equiv 0{\cdot}02533 \text{ g. } Cr_2O_3.$$

The above procedure may be applied also to the **separation of aluminium and chromium.**

Note. 1. The following reactions probably occur:

$$Cr_2O_3 + 3HClO_4 = 2CrO_3 + 3HClO_3;$$
$$3HClO_3 = HClO_4 + Cl_2 + 2O_2;$$
or
$$Cr_2O_3 + 2HClO_4 = 2CrO_3 + Cl_2 + 2O_2 + H_2O.$$

C. Manganese and zinc. This separation depends upon the solubility of manganese quinaldinate in dilute acetic acid, the corresponding zinc complex being insoluble.

Dissolve the mixture (1) in 200 ml. of water, heat, and add 2 ml. of glacial acetic acid. Treat the boiling solution slowly and with stirring with a slight excess of sodium quinaldinate reagent (Section **IV, 34C**). Allow the precipitate to settle, filter it through a weighed sintered glass or porous porcelain crucible, and wash successively with hot 1 : 40 acetic acid and hot water. Reserve the filtrate and washings (i). Dry the precipitate at 125°C to constant weight, and weigh as $Zn(C_{10}H_6ON_2)_2,H_2O$.

Determine the manganese in the filtrate (i) as the pyrophosphate (Section **IV, 35**).

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. manganese sulphate with A.R. zinc sulphate or pure zinc ammonium sulphate (Section **IV, 34A**).

D. Nickel and zinc. Weigh out accurately a suitable quantity of the mixture (1) containing not more than 0·2 g. of the total metals, dissolve it in 200 ml. of water, and add 1 ml. of concentrated hydrochloric or sulphuric acid. Heat the solution to boiling, add a large excess of the dimethylglyoxime reagent (Section **I, 62A**) followed by a concentrated solution of ammonium acetate until a precipitate appears and about 2 g. in excess. Digest for 30 to 60 minutes, and filter. Complete the estimation as in Section **IV, 12A.** Weigh as $Ni(C_4H_7O_2N_2)_2$. Reserve the filtrate and washings (i).

For the estimation of zinc it is necessary to destroy the excess of dimethylglyoxime. To do this, acidify the filtrate (i) with concentrated hydrochloric acid, and add 5 ml. of the concentrated acid in excess. Then introduce 25 ml. of concentrated nitric acid, and evaporate on a hot plate in the fume cupboard to dryness or to fumes of sulphur trioxide. Allow to cool, add 5 ml. of concentrated hydrochloric acid, warm the mixture, and dilute to 50 ml. Complete the determination as in Section **IV, 34A** (compare Section **IV, 89** (**f**))—remember that the proportions of the reagents apply to about 0·1 g. of Zn. Weigh as both the ammonium phosphate and the pyrophosphate.

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of pure (*e.g.*, A.R.) nickel ammonium sulphate and A.R. zinc sulphate.

E. Calcium and magnesium. The calcium is separated by double precipitation as calcium oxalate, whilst magnesium is determined by double precipitation as the ammonium phosphate. An alternative method which permits of the quantitative separation of the calcium in one operation is to precipitate it as calcium molybdate : magnesium is then determined in the filtrate as magnesium ammonium phosphate. For full experimental details, see Section **IV, 94D, E** and Section **IV, 94H** respectively.

A suitable mixture for practice may be prepared from A.R. calcium carbonate and A.R. magnesium sulphate.

F. Calcium and barium. This separation is based upon the difference in solubilities of calcium and barium chromates in acetic acid.

Weigh out a suitable quantity of the mixture (1), dissolve it in the minimum quantity of dilute hydrochloric acid in a covered beaker, boil to expel carbon dioxide, if present, and allow to cool. Neutralise with dilute ammonia solution, acidify with a few drops of acetic acid, and dilute to 50 to 100 ml. Introduce 10 ml. of a 30 per cent solution of A.R. ammonium acetate (this should be faintly ammoniacal), heat to boiling, and add dropwise and with constant stirring an excess of 10 per cent A.R. ammonium bichromate solution (5 to 10 ml.). Allow to cool for 1 hour, decant the clear yellow liquid through a quantitative filter paper (or through a porous porcelain crucible), and wash the precipitate by decantation with 2 per cent ammonium acetate solution until the filtrate is no longer perceptibly coloured (*ca.* 100 ml. of the wash liquid). Complete washing is unnecessary at this stage (2). Reserve the filtrate and washings (i). Transfer the precipitate by a jet of water from the wash bottle to the beaker containing the bulk of the precipitate, place the beaker under the funnel, and dissolve the residual precipitate in warm $2N$ nitric acid, and wash the filter with hot water until free from acid. Add more dilute nitric acid, if necessary, until the precipitate dissolves. Treat with 10 ml. of 30 per cent ammonium acetate solution, heat the liquid to boiling and stir steadily all the while, and allow to cool slowly during 1 hour. (The supernatant liquid should be yellow; if this is not the case, add a few ml. of ammonium bichromate solution.) Filter the precipitate through a weighed silica Gooch or porous porcelain crucible; wash first by decantation, then on the filter with 2 per cent ammonium acetate solution, and finally with cold water until the filtrate gives only a slight opalescence with 2 drops of $0{\cdot}1N$ silver nitrate. Reserve the filtrate and washings (ii). Dry the crucible and precipitate at 500° to 600°C or within a larger crucible at a dull red heat to constant weight. Weigh as $BaCrO_4$.

Treat the combined filtrates and washings (i and ii) with a little dilute nitric acid, evaporate to a small volume, and precipitate the calcium as carbonate by the addition of ammonia and A.R. ammonium carbonate solutions. Filter off the precipitate of calcium carbonate, wash it with a little hot water, dissolve it in the minimum volume of 1 : 1 hydrochloric acid, and precipitate the calcium as oxalate (Section **IV, 10**) and weigh either as $CaCO_3$ or as CaO, or precipitate as molybdate (Section **IV, 94H**) and weigh as $CaMoO_4$.

Notes. 1. For practice in this analysis, an intimate mixture of A.R. barium chloride and A.R. calcium carbonate may be employed.

2. The subsequent reprecipitation is unnecessary where results of only moderate accuracy are required. For the **separation of barium and strontium** this method may also be used, but reprecipitation is essential.

G. Calcium and strontium. The method (R. N. Shreve, C. H. Watkins and J. C. Browning, 1939) is based upon the fact that calcium nitrate is soluble in anhydrous acetone whilst strontium nitrate is almost insoluble (0·02 per cent at 25°C).

Weigh out a suitable quantity of the mixture (1), dissolve it in the minimum volume of dilute hydrochloric acid in a covered beaker, boil to expel carbon dioxide (if present), and allow to cool. Warm to 50°C, and precipitate the two elements as carbonates by the addition of excess of ammonia and A.R. ammonium carbonate solutions. Digest the precipitate on a steam bath or on a hot plate for 10 minutes, and allow to cool. Filter off the precipitate, and wash it with a little water. Dissolve the precipitate in dilute nitric acid, and evaporate the solution to dryness on a water bath. Allow to cool, add 25 ml. of anhydrous acetone, and cover with a clock glass ; leave the solvent in contact with the mixed nitrates for 1 hour with occasional agitation. Transfer the residual strontium nitrate to a weighed filter crucible, wash with more acetone, dry at 100°C, and weigh as $Sr(NO_3)_2$. Determine the calcium in the filtrate as $CaSO_4$ (the details are similar to those given under **H** below).

Note. 1. For practice in this analysis, an intimate mixture of known weights of A.R. strontium chloride or carbonate and A.R. calcium carbonate may be used.

H. Calcium, strontium, and barium. Although this analysis is hardly suitable for elementary students of gravimetric analysis, it is given here as an illustration of the separation and determination of three similar elements.

Precipitate the three elements as carbonates by the addition of excess of ammonia and A.R. ammonium carbonate solutions. Filter off the precipitate, and wash it with a little hot water. Dissolve the precipitate in dilute nitric acid, and evaporate the solution to dryness on the water bath ; heat for 30 minutes in an air bath (Section **II, 12F** or Fig. 2-13) at 135° to 140°C, and for 30 minutes at 180°C. Extract the powdered residue twice with 2·5 ml. portions of absolute ethyl alcohol, and once with 5 ml. of dry *iso*butyl alcohol (1). Dissolve the residue in water, evaporate to dryness on the water bath, and heat as above. Extract again with two 5 ml. portions of *iso*butyl alcohol. Evaporate the alcoholic filtrates cautiously in a weighed crucible (preferably of the Main-Smith type), and convert the residual calcium nitrate into calcium sulphate as follows. Add 1 or 2 drops of water, then 5 times the weight of finely-powdered A.R. ammonium sulphate, and dry at 100° to 110°C for 30 minutes. Place the crucible inside a larger porcelain crucible provided with an asbestos supporting ring (Fig. 60) and heat with a small flame until fuming commences, then increase the size of the flame. Continue the heating for 1/2 hour after all fuming has ceased. Allow the crucible to cool, and weigh as $CaSO_4$. (Too strong heating—above dull redness—causes loss of sulphur trioxide.)

Dissolve the residue containing the nitrates of strontium and barium in water or in dilute acetic acid, and determine the barium as chromate as detailed in **F.** Precipitate the strontium in the filtrate as the carbonate (the experimental procedure is similar to that given for calcium in **F**), filter, and wash with a little hot water ; dissolve the precipitate in a small volume of dilute hydrochloric acid and wash the filter with a little hot water. Add slowly a 10-fold excess of dilute sulphuric acid and then a volume of alcohol equal to that of the solution. Complete the determination as in Section **IV, 44A,** and weigh as $SrSO_4$. (Here also too strong heating—above dull redness—results in loss of sulphur trioxide.)

Note. 1. Commercial *iso*butyl alcohol is refluxed over dry baryta or over a little potassium hydroxide pellets, and then fractionated to separate the fraction of boiling point 107° to 108°C. Two drops should not give a cloudiness when mixed with 5 ml. of pure paraffin.

I. Sodium and potassium. The potassium in the mixture of chlorides is determined as potassium perchlorate and therefrom the equivalent amount of potassium chloride is computed. The sodium is obtained by difference. For experimental details, see Section **IV, 48, B, B′.**

A suitable mixture for practice may be prepared by intimately mixing A.R. sodium and potassium chlorides.

ANALYSES OF COMPLEX MATERIALS*

IV, 87. ANALYSIS OF BRASS

Discussion. The chief components of the alloy brass are copper and zinc, but small quantities of tin, lead and iron, and sometimes very small quantities of other elements as well, are usually present. The percentages of the important constituents rarely fall outside the following values :

Cu	Zn	Sn	Pb	Fe
50–90%	20–40%	0–6%	0–2%	0–1%. 3%

The analysis involves, therefore, the separation and determination of tin, lead, copper, iron, and zinc.

Outline of procedure. The sample is treated with nitric acid to precipitate the hydrated tin oxide SnO_2,nH_2O and to bring copper, zinc, iron and lead into solution : the insoluble stannic acid is filtered off, ignited and weighed as stannic oxide, SnO_2.† The filtrate from the tin precipitate is evaporated with an excess of sulphuric acid to fumes of sulphur trioxide in order to expel nitric acid. The residual liquid is treated with water, and the insoluble lead sulphate is filtered off, and weighed as $PbSO_4$ after ignition at about 500°C (see, however, Section **IV, 14A**). The copper in the filtrate from the lead sulphate is determined electrolytically by deposition on a platinum cathode, or is estimated as cuprous thiocyanate, $Cu_2(CNS)_2$. The solution from which the copper has been separated is treated with bromine water or with nitric acid to oxidise iron to the ferric state, and this metal is separated from the zinc by double precipitation with ammonia solution ; the ferric hydroxide is ignited and weighed as Fe_2O_3. Finally, the zinc is precipitated as zinc ammonium phosphate, and weighed either as zinc ammonium phosphate $ZnNH_4PO_4$ or, after ignition, as zinc pyrophosphate, $Zn_2P_2O_7$.

An alternative procedure for the electrolytic determination of lead by deposition as lead dioxide at the anode is described. If any antimony is present, it will be weighed with the tin ; any aluminium present will separate with the iron.

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* Space does not permit the inclusion of the experimental details for more than a few typical complex materials. For an excellent and authoritative account of many others the reader is referred to Lundell, Hofmann and Bright, *Chemical Analysis of Iron and Steel* (J. Wiley, 1931). This treatise contains details for *inter alia* iron ores ; manganese ores ; chrome ores ; fluor spar ; refractories of high alumina content and bauxite ; slags ; molding sands ; coal and coke ; spiegeleisen, ferromanganese and manganese metal ; ferrosilicon and refined silicon ; ferrochromium and chromium metal ; ferrovanadium ; ferromolybdenum and calcium molybdate ; ferrotungsten ; ferrocobalt and cobalt metal ; ferrotitanium ; ferrozirconium ; ferrotantalum ; and ferroboron. A standard reference work dealing with the analysis of complex materials is W. D. Scott-N. H. Furman, *Standard Methods of Chemical Analysis*, Vols. I and II (D. Van Nostrand Co. ; The Technical Press Ltd., 1939).

† Tin in brass, bronze, etc., may also be determined with phenylarsonic acid (see Section **IV, 220**).

Procedure. If the sample, which should be in the form of drillings or turnings, is not quite clean and dry, wash it with a little ether, and dry it by exposure to air on a watch glass for a short time.

(a) **Tin.** Weigh out accurately about 1 g. of the brass (1) into a 150 ml. beaker, add 10 ml. of water followed by 15 ml. of concentrated nitric acid ; keep the beaker covered with a clock glass or, better, a Fisher " speedyvap " beaker cover. When the vigorous reaction is over, evaporate on a water bath to a volume of 5 to 10 ml., but not to dryness. The evaporation should require at least an hour to insure that all the stannic acid has precipitated (2) ; longer digestion does no harm. Dilute to 50 ml., and heat on the water bath for 10 to 20 minutes in order that all soluble salts may dissolve. Then add one Whatman " accelerator," and stir. Filter hot through a small Whatman No. 42 or No. 542 paper, and collect the filtrate (i) in a 150 ml. beaker. (If the filtrate is not clear, refilter it, and add more macerated filter paper if the precipitate persists in running through.) Wash the precipitate at least 10 times with hot 1 per cent nitric acid solution. Fold up the filter paper and its contents into a weighed porcelain crucible, dry and char the filter at as low a temperature as possible, and finally ignite the residue for 30 minutes over a Méker or similar type burner under good oxidising conditions (compare Section **IV, 22A**). Allow to cool in a desiccator and weigh. Repeat the ignition until constant weight is obtained.

Calculate the percentage of tin in the sample.

If the residue is coloured, foreign oxides are present. The amount of stannic oxide present may be determined by the excellent ammonium iodide method (Section **IV, 22A**) or, less rapidly, by the following procedure. Mix the weighed residue with 8 times its weight of a mixture of equal parts of pure sodium carbonate and pure sulphur, cover the crucible with a lid, and heat with a low flame in the fume cupboard until the sulphur ceases to burn from under the crucible cover. Allow to cool, and then place the crucible and its cover in a beaker containing sufficient water to cover both, and warm to dissolve the melt. (During this process sodium polysulphide is formed, which reacts with the stannic oxide to give the soluble sodium thiostannate, and forms insoluble sulphides with the other metals. The latter sulphides, particularly that of copper, are appreciably soluble in polysulphide solutions, but not in solutions of normal sulphides ; hence it is necessary to decompose the polysulphide by the addition of sufficient sodium sulphite to form the colourless sulphide, for example :

$$Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S.)$$

After the melt has dissolved, remove the crucible and lid from the solution, and wash them free from the adhering solution. Then add excess of sodium sulphite solution, and boil for 10 to 15 minutes Filter off the residue, which may contain the sulphides of copper, lead and iron, through a quantitative filter paper, wash with 0·1*M* colourless ammonium sulphide solution, and ignite in a weighed porcelain crucible. The weight of the ignited residue, which may consist of CuO, PbO and Fe_2O_3, is subtracted from the weight of impure stannic oxide. The ignited residue should be dissolved in 1 to 2 ml. of 1 : 1 nitric acid, and added to the main filtrate containing the copper, lead and zinc.

Notes. 1. The determination should be conducted in duplicate. Ridsdale's "Brass, No. 5b" (one of the Analysed Samples for Students) is suitable for this estimation.

2. If no precipitate has appeared at the end of 1 hour, no appreciable quantity of tin is present.

(b) Copper and lead. There are three alternative methods of dealing with the main filtrate and washings from the tin separation (i). In *Method A* the lead is separated and weighed as lead sulphate, and the copper is separated and weighed as cuprous thiocyanate. In *Method B* the lead is separated as lead sulphate, and the copper determined electrolytically. In *Method C* both the lead and copper are determined electrolytically, the lead as lead dioxide at the anode and the copper as metallic copper at the cathode.

Method A. Add to the main filtrate (i) from the metastannic acid or, if tin was absent, to the nitric acid solution of the brass 3 to 4 ml. of concentrated sulphuric acid, and evaporate the solution carefully (*e.g.*, on a low temperature hot plate) until white fumes are evolved (3). Allow the solution to cool, wash down the sides of the beaker (or the casserole, if employed) with 10 to 20 ml. of water, and again evaporate to white fumes in order to insure the expulsion of all the nitric acid. Cool, add 25 ml. of water cautiously, heat nearly to boiling, and stir for several minutes until all soluble salts pass into solution. Then add 50 ml. of water, stir thoroughly, and allow to stand for at least 1 hour. Filter off the precipitate through a weighed silica Gooch or porous porcelain crucible, and wash thoroughly with cold 1 : 50 sulphuric acid. Reserve the filtrate and washings (ii). Ignite the lead sulphate to constant weight at 500° to 600°C (see Section **IV, 14A** in which other methods for weighing the $PbSO_4$ are described). Calculate the percentage of lead.

Evaporate the filtrate (ii) from the precipitation of lead sulphate to about 50 ml., almost neutralise the free acid with 1 : 1 ammonia solution, and precipitate the copper as cuprous thiocyanate (Section **IV, 19A**). Reserve the filtrate and washings (iii) for the determination of iron and zinc. Weigh as $Cu_2(CNS)_2$ after drying at 110° to 120°C.

Calculate the percentage of copper.

Method B. Determine the lead as lead sulphate as described under *Method A.* Concentrate the filtrate and washings (ii) from the lead sulphate to about 75 ml., add 4 ml. of concentrated ammonia solution to reduce the acidity, and then 2 ml. of concentrated nitric acid. Estimate the copper electrolytically ; use the slow or rapid method described in Section **IV, 78.**

The combined solution and washings (iii′) after the deposition of copper is kept for the determination of iron and zinc. It may contain a small amount of copper. This may be recovered by passing hydrogen sulphide into the solution for a few minutes. If only white sulphur is formed, copper is absent. If a small dark precipitate is formed, filter it through a small filter paper, wash with 1 per cent ammonium nitrate solution, and ignite to the oxide in a weighed porcelain crucible. Add the weight of copper contained in the cupric oxide to the weight obtained on the electrode. Evaporate the filtrate to remove hydrogen sulphide (iii), and use it for the determination of iron and zinc.

Method C. Evaporate the filtrate and washings from the metastannic acid (i) to 50 to 75 ml. Transfer quantitatively to an electrolytic beaker of 150 ml. capacity, add 1·5 ml. of concentrated nitric acid for each 10 ml. of solution, and then 0·5 ml. of concentrated sulphuric acid (to make the deposit more adherent). Introduce two clean and weighed electrodes into the solution. These may consist of a platinum gauze electrode (Fig. 4-10 *a*), which is connected to the positive terminal of the source of current, and a heavy platinum wire spiral (Fig. 4-8 *f*) or a platinum gauze electrode (Fig. 4-10 *b*), which is connected to the negative terminal and therefore acts as cathode. Alternatively, Sand's electrodes (Fig. 4-11 or Fig. 4-12), similarly connected, may be used. When all is ready, bring the 150 ml. beaker containing the solution beneath the electrodes, and adjust the height so that the electrodes extend nearly to the bottom, and the anode is at least three-quarters immersed. Switch on the current, and adjust the resistance to give 1·5 to 2 amps. at 2 volts (4). Electrolyse for 1·5 hours (5). Test for completeness of deposition by adding about 20 ml. of water, and observing whether any deposit is formed on the freshly immersed gauze or stem of the anode when the electrolysis is continued for 15 to 20 minutes. When the electrolysis is complete, lower the beaker gently or slowly raise the electrodes out of the solution whilst rinsing the electrodes thoroughly by a stream of water from a wash bottle, and take care that all the washings fall without loss into the electrolytic beaker ; the current should not be interrupted during the washing. When the electrodes are out of the solution and have been washed, turn off the current. Rinse the anode well in a beaker of water, then with acetone to remove water. Dry the anode at 220°C, cool in a desiccator, and weigh (compare Section **IV, 79**). Calculate the percentage of lead. Clean the electrode as described in Section **IV, 77.**

Some copper may have been deposited on the cathode. If this is the case, place the cathode in the electrolysed solution, and allow it to stand therein until the copper has been dissolved off. Then remove the cathode, rinse it with water, and reserve the solution for the determination of copper.

For the estimation of copper, it is necessary first to remove the large excess of nitric acid present in the solution. Add 3 ml. of concentrated sulphuric acid, and evaporate the solution until fumes of sulphur trioxide appear. Cool, dilute with water to 75 to 100 ml., add 2 ml. of concentrated nitric acid, and determine the copper as described in Section **IV, 78.** Calculate the percentage of copper. Reserve the liquid and washings (iii).

Notes. 3. Nitric acid increases the solubility of lead sulphate, and hence must be completely removed.

4. Excellent results are obtained by electrolysing overnight with 0·5 amp. at 2 volts.

5. Any of the electrodes shown in Figs. 4-7, 4-8, or 4-9 may be used.

(c) **Iron.** The exact procedure will depend upon whether the copper has been separated electrolytically (*Method B*) or as cuprous thiocyanate (*Method A*). In the former case the iron will be present in the ferrous state. In the latter case, the excess of thiocyanate and sulphite must be removed by evaporation with nitric and hydrochloric acids, which also removes ammonium salts.

Method D (**copper separated electrolytically**). Heat the solution (iii) from the electrolysis to boiling, add 3 to 4 ml. of saturated bromine water or 1 ml. of concentrated nitric acid, and boil for 2 to 3 minutes. Add concentrated ammonia solution until a precipitate is obtained, and then 10 ml. in excess. Allow the precipitate to settle, filter it through a small filter paper into a 400 ml. beaker, and wash the precipitate 3 times with 1 : 100 ammonia solution. Replace the

400 ml. beaker by the beaker in which the precipitation was made. Pour 20 ml. of hot 1 : 3 hydrochloric acid through the filter to dissolve the precipitate, wash the filter first with 1 : 100 hydrochloric acid and then with water to remove acid. Precipitate the iron in the filtrate as before, using 5 ml. excess of concentrated ammonia solution. Filter the precipitate through the same filter paper into the first filtrate, and wash the precipitate thoroughly with hot water containing a little ammonium nitrate and a drop or two of concentrated ammonia solution. Reserve the combined filtrates (iv) for the determination of zinc. Ignite the precipitate to ferric oxide (Section **IV, 8**) and weigh. Calculate the percentage of iron.

Method E (**copper separated as cuprous thiocyanate**). To the filtrate from the thiocyanate precipitation (iii) add 35 ml. of concentrated nitric acid and 15 ml. of concentrated hydrochloric acid, and evaporate the solution nearly to dryness. Treat the cold residue with 3 ml. of concentrated hydrochloric acid, warm to dissolve the residue, and dilute to 50 to 75 ml. If there is a precipitate (silica), filter it off on a small filter paper, and wash thoroughly with 1 : 100 hydrochloric acid. Determine the iron in the solution as in *Method D.*

(d) Zinc. This constituent of brass is usually determined by precipitation as zinc ammonium phosphate, which is subsequently ignited to and weighed as zinc pyrophosphate. Excessive amounts of ammonium salts must be removed by oxidising them with hydrochloric and nitric acids. If the thiocyanate method for copper was used, the ammonium salts were removed before the iron was separated. If, however, the lead or copper was determined electrolytically, the solution will contain a considerable quantity of ammonium salts. Remove them as follows. To the filtrate from the ferric hydroxide (iv) add 25 ml. each of concentrated hydrochloric acid and concentrated nitric acid, and evaporate the solution to dryness or to fumes of sulphur trioxide. Treat the cold residue with 3 ml. of concentrated hydrochloric acid, warm for a few minutes, dilute with water to 50 ml., and filter off any silica which may have separated, collecting the filtrate in a 400 ml. beaker.

Transfer the filtrate quantitatively to a 250 ml. volumetric flask, make up to the mark, and shake well. Remove 100 ml. of the solution,* add 5 g. of ammonium chloride, 10 ml. of

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* This volume contains about 0·1 g. of Zn.

$2N$ sodium acetate, and dilute to 140 ml. Heat on the water bath and, when hot, treat with 10 ml. of 10 per cent A.R. ammonium phosphate $(NH_4)_2HPO_4$ added slowly from a pipette or burette. Complete the determination as described in Section **IV, 34A.** Weigh the zinc first as $ZnNH_4PO_4$ after drying at 105°C for about 1 hour, and then as $Zn_2P_2O_7$ after ignition. Calculate the percentage of zinc. Finally, sum up the percentages of tin, lead, copper, iron and zinc.

Note. If the estimation of zinc has been spoilt because of some accident, it is desirable in a repeat analysis to avoid the time required for the separation of the other metals. The following method is applicable in the presence of large amounts of copper and small amounts of tin and lead, and is based upon the use of the tartrate ion to prevent the precipitation of the phosphates of these metals. Dissolve 1 g., accurately weighed, of brass in 30 ml. of 1 : 1 nitric acid, and *exactly* neutralise the solution with 1 : 5 ammonia solution, using litmus paper as indicator. Heat the solution to about 90°C, add 25 g. of ammonium tartrate dissolved in 75 ml. of water, heat again to 90°C, and add slowly and with constant stirring a solution of 7 g. of A.R. $(NH_4)_2HPO_4$ in 35 ml. of water. Keep the solution at 80° to 90°C for 1 hour, decant the supernatant liquid through a quantitative filter paper, transfer the precipitate to the paper, and wash it with 1 per cent ammonium tartrate solution. Dissolve the precipitate in 1 : 3 hydrochloric acid, and wash the filter first with 1 per cent hydrochloric acid and finally with water. Neutralise the filter and washings *very carefully* with 1 : 5 ammonia solution, using litmus paper, add 15 g. of ammonium tartrate dissolved in 50 ml. of water, and reprecipitate the zinc with ammonium phosphate.* Filter the precipitate through a weighed porous filtering crucible or through a silica Gooch crucible, and wash it with water. Ignite the zinc ammonium phosphate to the pyrophosphate in the usual way (Section **IV, 34A**).

IV, 88. ANALYSIS OF BRONZE

Discussion. The chief components of the alloy **bronze** are copper (60–97%) and tin (1–35%), but small amounts of lead, iron and zinc may be present. **Gunmetal** is composed nominally of 90% of copper and 10% of tin, but small amounts of zinc (up to 2%), lead and iron together with traces of phosphorus are always present. **Phosphor bronze** is similar in general composition to gunmetal, but contains also 0·2 to 1·5% of phosphorus and, sometimes, small amounts of antimony. **English bronze coins** contains about 95% of copper, 4% of tin, and 1% of zinc. **Aluminium bronze** usually consists of about 90% of copper and 10% of aluminium, but may also contain small amounts of iron and other metals. **Manganese bronze*** contains 55 to 60% of copper, 30 to 40% of zinc, 0 to 2% of tin, 0 to 1·5% of lead, 1 to 2% of iron, 0 to 3% of aluminium, and about 1% of manganese.

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* For the most accurate results, it is desirable to dissolve the precipitate and reprecipitate again.

Only the analysis of gunmetal and of phosphor bronze will be described here. The student should employ his own ingenuity in devising schemes for the analysis of the other bronzes, and should check up the procedure by reference to any of the standard text books on metallurgical analysis (see Appendix, Section **A, 3**).

For the analysis of gunmetal and of phosphor bronze, the experimental details are similar to those already given under Brass (Section **IV, 87**) for the determination of copper, lead, iron and zinc. The precipitated metastannic acid will carry down considerable quantities of lead, copper and iron, and also phosphorus, if present, presumably as stannic phosphate. It is therefore essential to determine the amount of tin present in the impure precipitate. Three methods may be used.

Method A. Transfer the precipitate of metastannic acid and macerated filter paper to a beaker, add 10 ml. of ammonium hydrogen sulphide (NH_4HS) solution, prepared by saturating concentrated ammonia solution with hydrogen sulphide, and warm until the precipitate largely dissolves. The sulphides of copper, lead and iron will remain unattacked. Filter through a hardened quantitative filter paper, and wash with dilute ammonium hydrogen sulphide water. Dissolve the sulphides on the paper in a small volume of 1 : 1 nitric acid and a little bromine water, and add the solution to the main filtrate from the metastannic acid. Heat the ammonium sulphide solution of tin to boiling until a precipitate commences to form, add 10 to 15 ml. of concentrated nitric acid, and evaporate to dryness. Add 50 ml. of 1 : 10 nitric acid, heat to boiling, add one Whatman accelerator, filter through a Whatman No. 42 or No. 542 paper, and wash the precipitate with 1 per cent nitric acid. Complete the estimation as described in Section **IV, 87 (a)**, and weigh the tin as stannic oxide.

Method B. Ignite the impure metastannic acid, and weigh as $SnO_2 + P_2O_5 +$ foreign oxides. Heat the impure weighed oxides with a large excess of ammonium iodide at 425° to 475°C, treat the residue with nitric acid, ignite and weigh. By subtracting the latter weight from that previously obtained, the weight of $(SnO_2 + P_2O_5)$† is secured. A separate portion is analysed for phosphorus (see below) and the weight of P_2O_5 is subtracted from that of $(SnO_2 + P_2O_5)$. If phosphorus is absent, the method is of course much simplified.

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* This is sometimes termed high tensile brass.

† See Section, **IV, 22A.** The phosphorus and stannic tin are volatilised as the iodides. The residue in the crucible may be dissolved in hot concentrated hydrochloric acid, and added to the main filtrate for the determination of the other metals.

Method C. Transfer the precipitate of metastannic acid and macerated filter paper, preferably dried at 100°C, to a Kjeldahl flask (see Section **III, 20**), treat with 15 ml. of concentrated sulphuric acid and 5 g. of anhydrous sodium sulphate, and boil gently until the organic matter is destroyed. Dilute cautiously, transfer to a flask fitted with carbon dioxide tubes (Section **III, 116**, *Procedure* B), add 2 to 3 g. of pure lead, excess of concentrated hydrochloric acid, and boil gently in an atmosphere of carbon dioxide. The quadrivalent tin is reduced by the lead to the bivalent state :

$$SnCl_4 + Pb + 2HCl = SnCl_2 + PbCl_2 + 2HCl.$$

Allow to cool in a stream of carbon dioxide, and then titrate the stannous tin with standard iodine solution (Section **III, 116**, *Procedure B*). From the volume of standard iodine solution required, calculate the percentage of tin.

For the determination of the other metals, treat another sample of the alloy with 1 : 1 nitric acid, etc., and dissolve the impure metastannic acid in a mixture of concentrated sulphuric acid and sodium sulphate as above. Transfer the mixture quantitatively to a beaker, treat cautiously with excess of sodium hydroxide solution followed by excess of sodium sulphide, and digest for some time. The tin thus passes into solution as sodium thiostannate Na_2SnS_3, and the sulphides of the other metals (*e.g.*, iron, copper, zinc, etc.) are precipitated. Allow to cool, dilute somewhat, and filter. Dissolve the residue in hot 1 : 1 nitric acid, and add the solution to the main filtrate for the estimation of the other metals.

Analysis of gunmetal. *Procedure.* Use 0·5 to 1 g., accurately weighed, of the clean dry alloy (1), and proceed as detailed in Section **IV, 87** for Brass. The tin should be determined by any of the three methods given above, but preferably by *Method B* (2). Finally, sum up the percentages of tin, copper, lead, iron and zinc in the sample.

Notes. 1. Ridsdale's " Gunmetal, No. 6b " (one of the Analysed Samples for Students) is suitable for this analysis.

2. Perhaps the simplest method for the determination of tin is with phenylarsonic acid (Section **IV, 22C.**)

Analysis of phosphor bronze. *Procedure.* Use 0·5 to 1 g., accurately weighed of the alloy (3), and follow the method used for gunmetal (4). Determine the **phosphorus** in a fresh sample as follows.

Weigh out accurately about 2 g. of the sample into a 300 to 350 ml. conical flask, and dissolve it in 20 to 25 ml. of aqua regia. When all the alloy has dissolved, add 10 ml. of water, and digest at 90°C for 10 minutes. Dilute to 50 to 60 ml., and adjust the temperature to 40° to 50°C. Add 100 ml. of the ammonium molybdate reagent, previously heated to 40° to

50°C, slowly and with constant stirring. Complete the estimation as described in Section **IV, 65B.** Dissolve the precipitated ammonium phosphomolybdate in 5*N* ammonia solution, and precipitate the phosphate with magnesia mixture as magnesium ammonium phosphate. Ignite the latter and weigh as magnesium pyrophosphate. From the weight of the latter, calculate the percentage of phosphorus in the sample.

Finally, sum up the percentage of tin, copper, lead, iron, zinc and phosphorus in the phosphor bronze.

Notes. 3. Ridsdale's " Phosphor Bronze, No. 7 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Bronze ' A ' " (one of the British Chemical Standards) is suitable for this analysis.

4. If the ammonium iodide method for tin is used, it must be remembered that both tin and antimony (the latter is often present in samples of phosphor bronze) are volatilised. The tin alone may be determined by the phenylarsonic acid method (Section **IV, 22C**), or by *Method C* (above), and hence the antimony content estimated by difference.

IV, 89. ANALYSIS OF GERMAN SILVER (NICKEL SILVER)

Discussion. The chief components of German silver are copper (46–63%), zinc (20–34%), and nickel (6–25%) ; small quantities of iron, lead and tin may also be present. The procedure described allows for the determination of all these elements and is given in outline only since most of the essential details have already been given under Brass (Section **IV, 87**).

Procedure. Weigh out accurately about 0·5 g. of German silver in the form of clean drillings or turnings into a tall 150 to 200 ml. beaker. Cover the beaker and add slowly 10 ml. of concentrated nitric acid. When the reaction is almost over, warm the mixture on a hot plate until the alloy has completely dissolved. Add 10 ml. of water, and allow the solution to digest for 10 to 15 minutes.

(a) Tin. If a white residue is present, it is metastannic acid. This should be separated and determined according to the procedure for tin in Brass (Section **IV, 87 (a)**).

(b) Lead. Add 2 to 3 ml. of concentrated sulphuric acid to the filtrate from the metastannic acid or, if tin is absent, to the original solution. Evaporate the solution to a pasty mass and fumes of sulphur trioxide (*not to dryness*) to remove all the nitric acid. To the cold residue add 30 ml. of water cautiously, stir thoroughly, and allow to stand for at least an hour in order that the precipitation of lead sulphate may be complete. From this point follow the experimental details given for lead in *Method A* under Brass.

(c) **Copper.** The filtrate from the lead sulphate, or the original solution if both tin and lead are absent, is employed for the electrolytic determination of copper. Determine the copper electrolytically ; use either the slow or rapid method described in Section **IV, 78** (see *Method B* in Section **IV, 87** (**b**)).

(**d**) **Iron.** Add 1 to 2 ml. of hydrogen peroxide to the solution from the copper determination in order to reoxidise the iron to the ferric state. Add a large excess of concentrated ammonia solution, and heat to boiling. Filter off the precipitated ferric hydroxide, and wash it with hot water. Dissolve the precipitate in the minimum volume of hot 1 : 1 hydrochloric acid, and receive the acid solution in a small beaker. Pour in enough 1 : 2 ammonia solution to reprecipitate the ferric hydroxide, heat to boiling, filter and wash the precipitate. Add the filtrate and washings to the main filtrate containing the zinc and nickel. Ignite the precipitate, and weigh the ferric oxide.

(**e**) **Nickel.** Add hydrochloric acid to the combined filtrates from the determination of iron until neutral (to litmus paper), and add 5 ml. in excess. Add ammonia solution slowly until the solution is faintly ammoniacal. Ammonium chloride is formed by this neutralisation process and this must be present in order to hold the zinc in solution ; the same result is achieved by adding 5 g. of ammonium chloride to the faintly ammoniacal solution. For each 0·1 g. of nickel that is expected to be present, add to the hot solution 0·5 g. of dimethylglyoxime (1) dissolved in rectified spirit, and make certain that the solution is slightly ammoniacal (add more dilute ammonia solution, if necessary). Allow the beaker to stand on the steam bath for 15 to 20 minutes, and test the solution for complete precipitation after the red precipitate has settled out. Complete the determination as described in Section **IV, 12A.**

Note. 1. Too large an excess of dimethylglyoxime must be avoided as otherwise it, too, may be precipitated.

(**f**). **Zinc.** Acidify the filtrate from the determination of nickel with concentrated hydrochloric acid, and add 5 ml. of the concentrated acid in excess. Then add 25 ml. of concentrated nitric acid, and evaporate on a hot plate in the fume cupboard either to dryness or to fumes of sulphur trioxide if much sulphuric acid is present. This evaporation removes the organic matter and the large amount of ammonium salts present in solution. Treat the cold residue with 5 ml. of concentrated hydrochloric acid, warm the mixture for a few minutes, dilute to 50 ml., and, when the salts have dissolved, filter the solution if not perfectly clear. Complete the determination as described for zinc in Brass (Section **IV, 87** (**d**)). Weigh the zinc as both the ammonium phosphate and as the pyrophosphate.

IV, 90. ANALYSIS OF SOLDER

Discussion. Ordinary solder is an alloy of approximately 3 parts of lead and 2 parts of tin, but it usually contains also from 1 to 3 per cent of antimony as impurity. When such an alloy is disintegrated by nitric acid, the insoluble residue consists of metastannic acid and antimonic acid, together with some coprecipitated lead compound. The ignited residue will consist of $SnO_2 + Sb_2O_4 + PbO$. The amount of lead present in the residue is most simply determined by the ammonium iodide volatilisation method (Section **IV, 22A**) ; the tin and antimony are volatilised as the iodides, and the lead remains behind as a mixture of oxyiodide and oxide. The residue in the crucible is treated with 2 to 3 ml. of concentrated nitric acid (a Main-Smith crucible is very suitable for this process), evaporated to dryness on the hot plate, the nitrate cautiously decomposed, and finally ignited to oxide at a low red heat. The loss in weight gives $(SnO_2 + Sb_2O_4)$. The tin may be determined as in *Method C*, Section **IV, 88** (antimony does not interfere with this process), and the antimony obtained by difference. The residual PbO in the crucible may be dissolved in a little concentrated hydrochloric or nitric acid, and added to the main filtrate from the metastannic acid. The lead is determined as sulphate (Section **IV, 14A**) or as chromate (Section **IV, 14B**) ; in the latter case, about 12 g. of sodium acetate are added to replace the free nitric acid by acetic acid.

An alternative procedure is to transfer the impure metastannic acid precipitate and filter paper, preferably dried at 100°C, to a Kjeldahl flask, add a mixture of 20 ml. of concentrated sulphuric acid and 5 g. of anhydrous sodium sulphate, and the whole boiled gently until the organic matter is destroyed. The carbonaceous matter from the filter paper reduces the antimony to Sb^{III}. The mixture is evaporated to fumes of sulphur trioxide, allowed to cool, cautiously transferred quantitatively to a conical flask with the aid of about 50 ml. of water, concentrated hydrochloric acid, cooled to 10°C, and titrated with standard $0{\cdot}1N$ potassium permanganate (see Section **III, 117** :

$$\begin{aligned}5Sb_2(SO_4)_3 + H_2SO_4 + 4KMnO_4 + 4H_2O \\ = 10H_3SbO_4 + 2K_2SO_4 + 4MnSO_4 + 10H_2SO_4.\end{aligned}$$

The percentage of antimony can then be calculated. Excess of concentrated hydrochloric acid is then added, followed by 2 to 3 g.

of pure lead, and the mixture boiled gently in an atmosphere of carbon dioxide (see *Method C* in Section **IV, 88**). The quadrivalent tin is reduced by the lead to the bivalent state, and the antimony is precipitated as the metal. The stannous tin is titrated with standard 0·1*N* iodine, and from the volume of the latter required the percentage of tin may be calculated (Section **III, 117**).

The procedure is much simplified if antimony is absent, as in the case of a pure solder or a pure lead-tin alloy. Such alloys are available commercially, and are useful for practice in the quantitative separation and determination of lead and tin. Here the amount of lead oxide present in the impure stannic oxide may be determined either by the ammonium iodide process or by the sodium carbonate-sulphur fusion process (Section **IV, 87 (a)**). The lead is determined in the filtrate from the impure metastannic acid, to which the small amount of recovered lead has been added, as the sulphate.

Analysis of pure solder or a pure lead-tin alloy. *Procedure.* Weigh out accurately about 0·5 g. of the finely-divided alloy (turnings, drillings, etc.)(1) into a 150 to 200 ml. beaker, and cover with a clock glass or Fisher " speedyvap " cover. Add 5 ml. of water, followed by 15 ml. of concentrated nitric acid : keep the beaker covered during the ensuing violent reaction. When the vigorous reaction is over, evaporate on a water bath to a volume of about 5 ml., but not to dryness. Dilute to 50 ml., heat on a water bath for 10 to 15 minutes, then add one Whatman accelerator (or half of an ashless tablet), and stir. Filter through a Whatman No. 42 or No. 542 paper, and collect the filtrate in a 250 to 400 ml. beaker. Wash the precipitate at least 10 times with 1 per cent nitric acid. Keep the filtrate and washings for the determination of lead. Fold up the filter paper and precipitate and place it in a weighed porcelain crucible (best in a Main-Smith crucible), and complete the estimation as described for Tin in Section **IV, 87 (a)**. Weigh the impure stannic oxide. Add to the latter about 15 times its weight of powdered ammonium iodide, and mix the two in the crucible intimately by means of a small spatula. Heat the crucible in an electric crucible or muffle furnace at 425° to 475°C. for 15 minutes or until no further fumes are evolved. Allow the crucible to cool, remove it, and add 2 to 3 ml. of concentrated nitric acid. Evaporate gently to dryness, and cautiously decompose the residual nitrate over a small flame. Then ignite at a low red heat to constant weight. The loss in weight gives the weight of pure stannic oxide present in the residue. Calculate the percentage of tin.

Dissolve the residue in the crucible by digestion with a few ml. of concentrated hydrochloric acid, and add it to the filtrate and washings from the metastannic acid. Add 7 to 8 ml. of concentrated sulphuric acid, and evaporate the solution carefully (*e.g.*, on a low temperature hot plate) until white fumes of sulphur trioxide are freely evolved. Complete the determination of lead as sulphate according to the procedure given for Lead in Section **IV, 87** (**b**) (*Method A*). Calculate the percentage of lead.

Note. 1. Ridsdale's " Solder, No. 11a " (one of the Analysed Samples for Students) is an almost pure lead-tin alloy, and is suitable for this analysis.

IV, 91. ANALYSIS OF A SILVER COINAGE ALLOY

Discussion. Prior to 1920 British silver coins contained from 90 to 95 per cent of silver, the remainder being copper ; subsequently the percentage of silver was reduced to 50 and this was alloyed with nickel and copper. Many silver coinage alloys also contain a little zinc ; the procedure to be described will therefore permit of the separation and determination of silver, copper, nickel and zinc.

Procedure. The alloy should be clean and grease-free. If dirty, the surface may be cleaned with a little fine emery paper or cloth, and then washed with dry acetone. The coin or sheet of alloy may be cut with the shears into pieces, each weighing 0·4 to 0·5 g.

(**a**) **Silver.** Weigh out accurately about 0·4 g. of the alloy into a 600 ml. beaker, which is covered with a clock glass. Add 5 ml. of water, and then concentrated nitric acid slowly (5 to 10 ml.). Warm on a water bath or upon a low temperature hot plate until solution is complete (the minimum quantity of nitric acid required for dissolution should be used). Dilute to 300 ml., heat to 70°C, and add approximately $0{\cdot}2N$ hydrochloric acid dropwise and with constant stirring until precipitation is complete. Complete the determination as in Section **IV, 15,** and weigh the silver chloride. Reserve the filtrate and washings (i).

(b) **Copper.** Add 3 to 4 ml. of concentrated sulphuric acid to the combined filtrate and washings (i) from the silver estimation, and evaporate until dense fumes of sulphur trioxide appear. Allow the solution to cool, wash down the sides of the vessel with 10 to 20 ml. of water, dilute to 100 ml., and almost neutralise the solution with 1 : 1 ammonia solution. Then add 5 ml. of cold, freshly-prepared, saturated sulphurous acid solution, followed by 10 per cent ammonium thiocyanate solution slowly and with constant stirring from a burette until present in slight excess (*ca.* 10 ml.). Complete the estimation as in Section **IV, 19A,** and weigh the precipitate as cuprous thiocyanate. Keep the filtrate and washings (ii) for the estimation of nickel and zinc.

(c) **Nickel.** Evaporate the combined filtrate and washings (ii) to 50 ml., add 35 ml. of concentrated nitric acid and 15 ml. of concentrated hydrochloric acid, and evaporate the solution nearly to dryness. This will destroy the excess of thiocyanate. Rinse the clock glass, and evaporate to dryness on the water bath in order to expel the excess of nitric acid. Add 1 ml. of concentrated hydrochloric acid, 150 ml. of water, and 5 g. of ammonium chloride (to retain the zinc in solution), and then 1 : 1 ammonia solution until slightly ammoniacal. Precipitate the nickel as the dimethylglyoxime complex ; follow the procedure given under German silver (Section **IV, 89** (**e**)).

(**d**) **Zinc.** Determine the zinc as the ammonium phosphate and the pyrophosphate exactly as described in Section **IV, 89** (**e**).

Finally, sum up the percentages of silver, copper, nickel, and zinc (if present).

IV, 92. ANALYSIS OF STEEL

Discussion. Plain carbon steel contains a certain amount of carbon, silicon, sulphur, phosphorus, and manganese. For special purposes, varying amounts of other elements, such as chromium, vanadium, molybdenum, tungsten, titanium, nickel,cobalt,zirconium and copper, are added. Iron itself is rarely determined in steel; only the subsidiary elements are estimated, for these are of great practical importance. Generally a number of methods are available for the determination of each element. The procedure employed will depend upon the object in view ; the more accurate methods are usually less rapid. In this book only a selected number of exact methods for determining the most important elements which are found in steel will be described. For a more detailed treatment of the subject, the reader is referred to the numerous special works on iron and steel analysis (see Appendix).

Procedure. **A. Carbon.** The total carbon in steel is determined by combustion at 1000° to 1300°C in an atmosphere of pure oxygen. The gases resulting from the combustion (CO_2, SO_2 and SO_3) are passed through reagents which absorb everything but oxygen and carbon dioxide, and the carbon dioxide is finally absorbed in a U-tube containing a suitable solid reagent (see Section **IV, 76**).*

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* For full experimental details the reader is referred to any of the standard text books on the subject, *e.g.*, Lundell, Hofmann, and Bright, *Chemical Analysis of Iron and Steel* (J. Wiley, 1931) or to *Sampling and Analysis of Carbon and Alloy Steels* (Rheinold Publishing Co., 1938).

B. Phosphorus. This element occurs as phosphide, and must be oxidised to orthophosphate before it can be determined. Weigh out accurately about 3 g. of the steel (1) into a 250 ml. conical flask, add 75 ml. of 6*N* (3 : 8) nitric acid, and warm gently on a hot plate until the solid has dissolved. Then add 20 ml. of 2 per cent potassium permanganate solution, and boil for a few minutes in order to precipitate the manganese dioxide ; add more permanganate solution if no precipitate appears. Dissolve the precipitate by adding a freshly prepared solution of sodium sulphite dropwise ; boil for a few minutes to expel sulphur dioxide and oxides of nitrogen. Partially neutralise the nitric acid by the addition of 20 to 25 ml. of 6*N* ammonia solution, and then introduce 75 ml. of ammonium molybdate reagent. Stopper the flask with a rubber bung, and shake for 5 minutes. Wash off the stopper, and allow to stand for 2 hours, or preferably overnight. Filter off the precipitate of ammonium phosphomolybdate, and wash it moderately with 5 per cent ammonium nitrate solution. Dissolve the precipitate in 20 ml. of 6*N* ammonia solution containing 2 g. of citric acid, and collect the filtrate in a 250 ml. beaker. Wash the filter paper 2 to 3 times with 1 : 20 ammonia solution, and finally twice with 1 : 20 hydrochloric acid. Add a few drops of methyl red, and acidify the solution with dilute hydrochloric acid. Next add 25 ml. of magnesia mixture (Section **IV, 20B,** Note 2). Complete the estimation as in Section **IV, 65B,** and weigh the precipitate as magnesium pyrophosphate.

Note. 1. Any of the following samples are suitable for this estimation: Ridsdale's " Medium Carbon Steel, No. 2 " (one of the Analysed Samples for Students) ; the Bureau of Analysed Samples " Carbon Steel, ' P ' or ' S^1 ' " (British Chemical Standards) ; British Standardised Steel Sample, No. 3 (supplied by the National Physical Laboratory, Metallurgy Department, Teddington, Middlesex, England).

B. Sulphur. Two methods for the determination of sulphur in steels are generally employed. In the first, the sulphur is ultimately weighed as barium sulphate, and is the more accurate. In the second, the hydrogen sulphide evolved by the action of hydrochloric acid, is absorbed in an ammoniacal solution of cadmium chloride or of zinc sulphate, and the precipitated sulphide is titrated in an acid medium with standard iodine solution in the presence of starch as indicator. The volumetric method tentatively assumes that the sulphur is present in the form of sulphide, and that all the sulphur is evolved as hydrogen sulphide upon treatment with acid.

This is not always entirely the case so that the procedure is not as accurate as the gravimetric method, but owing to its greater rapidity it is very often used, particularly for routine work. The accuracy of the method may be increased by standardising the iodine solution against a steel of known sulphur content similar in characteristics to the sample being analysed. For further details, consult any good text book on Metallurgical Analysis (see Appendix, Section **A, 3**).

Procedure. **Gravimetric method.** Weigh out accurately about 5 g. of the steel (1) into a covered 350 ml. conical flask or beaker. Add 50 ml. of pure concentrated nitric acid. Warm, if necessary, on the steam bath until the sample is dissolved : the cautious addition of up to 5 ml. of concentrated hydrochloric acid will facilitate solution in cases where difficulty arises. When the sample has dissolved, add 1 g. of A.R. sodium chloride (2), evaporate to dryness, and bake gently on a hot plate for about 10 minutes (3). Cool, add 25 ml. of concentrated hydrochloric acid, and evaporate the solution almost to dryness (*i.e.*, until syrupy). Then add 5 ml. of concentrated hydrochloric acid, 25 ml. of water, and 5 g. of A.R. (sulphur free) zinc granules (4). Warm on the steam bath until all the ferric iron has been reduced and evolution of hydrogen ceases. Filter the solution through a small filter, and collect the filtrate in a 250 to 400 ml. beaker. Wash the residue with small volumes of 1 : 50 hydrochloric acid (use about 50 ml. in all). Warm the filtrate and washings to 70°C, and precipitate the sulphate by the slow addition of 10 ml. of hot 10 per cent barium chloride solution. Allow to stand overnight, and filter through a Whatman No. 40 or No. 540 filter paper. Wash first with a solution containing 10 ml. of concentrated hydrochloric acid and 1 g. of barium chloride per litre, then with cold water to remove chlorides (50 to 75 ml.). Ignite and weigh the precipitate as barium sulphate according to the procedure of Section **IV, 6.** For the best results a platinum crucible should be used ; the ignited residue should be treated with 1 drop of concentrated sulphuric acid and 1 ml. of pure (*e.g.*, A.R.) hydrofluoric acid, evaporated to dryness, and ignited again to constant weight.

Notes. 1. Any of the following samples are suitable for practice in this estimation : Ridsdale's " Medium Carbon Steel, No. 2 " (one of the Analysed Samples for Students) ; the Bureau of Analysed Samples " Carbon Steel, 'H¹' or 'R' " (British Chemical Standards) ; British Standardised Steel Sample, No. 1 or No. 2 (supplied by the N.P.L.)—see Appendix, Section **A, 8.**

2. The addition of sodium chloride will fix sulphuric acid as sodium sulphate.

3. The nitric acid must be removed, because of the serious coprecipitation of nitrates in the subsequent precipitation of barium sulphate (see Section **IV, 6**).

4. Ferrous and zinc chlorides are not carried down to any serious extent by barium sulphate : ferric chloride is coprecipitated if present in appreciable concentration.

C. Silicon. The steel may be dissolved in nitric acid, dilute sulphuric acid, or in a mixture of nitric and sulphuric acids ; the silica is rendered insoluble and purified with the aid of hydrochloric acid as already described (Section **IV, 70**). The best procedure is to employ 60 to 70 per cent perchloric acid for dehydrating the silica ; with this acid the silica is more readily filtered, and is practically free from impurities since the perchlorates of the metals are generally very soluble. Both methods will be given.

Method 1. Weigh out accurately about 5 g. of the steel (1) into a porcelain dish or casserole, and cover it with a clock glass. Add carefully 100 ml. of a mixture of 35 parts of concentrated nitric acid, 15 parts of concentrated sulphuric acid and 50 parts of water. Warm until reaction ceases. When the sample has dissolved, evaporate the solution until dense fumes of sulphur trioxide are evolved for 2 to 3 minutes ; take precautions to avoid spattering. Allow to cool, add 10 ml. of concentrated hydrochloric acid, and wash off the cover into the dish. Treat with 150 ml. of water at 40°C, warm, but do not boil, to dissolve the salts. Filter at once through a Whatman No. 40 or No. 540 paper ; use a rubber policeman to dislodge any particles adhering to the sides of the vessel. Wash the precipitate with cold 1 : 20 hydrochloric acid until the ferric salts have been removed, and then several times with hot water. Place the paper and precipitate in a weighed platinum crucible, heat slowly to char the paper and burn off the carbon, and then apply the full heat of a Méker type of burner. Ignite to constant weight. In accurate work the weight of pure SiO_2 present in the residue should be ascertained by treatment with a little concentrated sulphuric and hydrofluoric acids (for details, see Section **IV, 70**).

Method 2. Weigh out accurately about 2·5 g. of the steel into a 400 ml. beaker, provided with a clock glass cover. Add 40 ml. of 6*N* nitric acid. When the sample has dissolved, rinse and remove the glass cover, add 25 to 30 ml. of A.R. 60 to 70 per cent perchloric acid (**DANGER,** see Section **IV, 70**), and evaporate on a hot plate to copious fumes of perchloric acid. Replace the cover on the beaker, and heat so that the perchloric acid condenses and runs down the sides of the beaker for 15 minutes. Do not allow the contents of the vessel to become pasty or solid, since if this occurs the separation of silica is always incomplete ; add more perchloric acid, if necessary. Allow to cool somewhat, dilute with 125 ml. of hot water, and heat to boiling. Filter off the precipitated silica, and complete the determination as in *Method I.*

Note. 1. The same sample as was employed for the estimation of sulphur may be employed, except that British Standardised Steel Sample, No. 12 (Cast Iron Standard Sample for Si, P, Mn and S) be utilised.

D. Manganese. This element is usually determined by the bismuthate process (Section **III, 60**). For practice in this estimation, the student may employ the same sample of steel as was employed for Silicon.

E. Nickel. This element is nearly always determined by precipitation with dimethylglyoxime. Full experimental details are given in Section **IV, 12B.**

F. Chromium. All methods for determining chromium in alloys are based upon the oxidation of the element to the chromate, followed by the determination of the latter by volumetric methods. Chromium is usually associated with vanadium in steels, and a procedure for the estimation of both elements is given under Vanadium. Two methods for chromium will be described here ; they are applicable both to Cr-V steels and to ferro-chromium.

Method 1. Weigh out accurately about 2 g. of the Cr-V steel (1), in the form of turnings or drillings, into a 600 ml. beaker, and dissolve it in 60 ml. of a solution containing 45 ml. of water, 12 ml. of concentrated sulphuric acid and 3 ml. of pure syrupy phosphoric acid (2). Heat until effervescence nearly ceases, then add 5 ml. of concentrated nitric acid (3), and boil until solution is complete and oxides of nitrogen are expelled. If any residue of tungstic acid appears, filter it off, and wash it thoroughly with dilute nitric acid. Dilute to about 250 ml., and add 10 to 15 ml. of 0·1*N* silver nitrate and 15 ml. of a freshly-prepared 8 per cent ammonium persulphate solution, and boil (4). If a permanganate colour does not develop at first from the manganese in the steel, add more silver nitrate and ammonium persulphate solutions. Continue the vigorous boiling for 8 minutes to decompose the excess of persulphate (5). Then add 2 ml. of 1 : 1 hydrochloric acid, and boil for 10 minutes after the permanganate colour, or any precipitated manganese dioxide, has disappeared : any chlorine present is thus removed. Cool, dilute to 400 ml., add $0{\cdot}1N$ ferrous ammonium persulphate until all the yellow colour disappears, thus indicating the complete reduction of the chromic and vanadic acids (6), and add a further 10 ml.: note the exact volume of ferrous solution added. Titrate the excess of ferrous solution with standard $0{\cdot}1N$ potassium permanganate until a faint pink colour is obtained which persists for 1 minute with constant stirring (7). From the volume of ferrous solution used, calculate the percentage of Cr in the sample of steel.

Notes. 1. The Bureau of Analysed Samples "Chromium-Vanadium Steel 'V'" is suitable for practice in this determination. If ferro-chromium is used (see *Method 2*), only about 0·25 g. should be weighed out.

2. The object of the phosphoric acid is to decolourise the iron salts that are formed.

3. Evaporation with nitric acid is necessary in order to break up the black insoluble carbides of chromium and vanadium which are left after the non-oxidising attack with the mixed acids.

4. Persulphate oxidises chromium in the presence of silver nitrate(catalyst)

$$(Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 6H_2O = 2H_2CrO_4 + 3(NH_4)_2SO_4 + 6H_2SO_4),$$

any unoxidised vanadium

$$(2(VO)SO_4 + (NH_4)_2S_2O_8 + 6H_2O = 2H_3VO_4 + (NH_4)_2SO_4 + 3H_2SO_4)$$

and manganese

$$(2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O = 2HMnO_4 + 5(NH_4)_2SO_4 + 7\,H_2SO_4).$$

5. $$2(NH_4)_2S_2O_8 + 2H_2O \xrightarrow[\text{heat}]{} 2(NH_4)_2SO_4 + 2H_2SO_4 + O_2.$$

Partial decomposition of the permanganic acid also occurs:

$$4HMnO_4 + xH_2O \rightarrow 4MnO_2, y\,H_2O + 3O_2.$$

6. $$2H_2CrO_4 + 6H_2SO_4 + 6FeSO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O;$$
$$2H_3VO_4 + 3H_2SO_4 + 2FeSO_4 = V_2O_2(SO_4)_2 + Fe_2(SO_4)_3 + 6H_2O.$$

7. In the back titration with permanganate solution, the reduced vanadium is reoxidised;

$$2KMnO_4 + 10(VO)SO_4 + 22H_2O = K_2SO_4 + 2MnSO_4 + 10H_3VO_4 + 7H_2SO_4,$$

as is also the excess of ferrous solution. It is therefore clear that the sole function of the permanganate solution is to react with the excess of ferrous iron and of the vanadium that has been reduced, and consequently if the permanganate and ferrous solutions are of equal normality, the difference between the volumes used represents the volume of ferrous ammonium sulphate solution required to reduce the chromic acid formed from the chromium present in the sample.

Method 2. Weigh out accurately about 0·2 g. of ferro-chromium (8) into a tall 600 ml. beaker, add 20 ml. of concentrated hydrochloric acid, cover with a clock glass, and heat for 15 minutes. Add 20 to 25 ml. of pure 60 to 70 per cent perchloric acid (**DANGER,** see Section **IV, 70),** and boil for 30 minutes after the hydrochloric acid has been expelled. Cool somewhat, add a few ml. of water to dissolve the chromium trioxide, and reoxidise by boiling for 15 minutes after the water is expelled. If any undissolved particles of metal remain, pour off most of the solution, add a few ml. of 60 to 70 per cent perchloric acid to the residue, and boil until solution is complete. Add the main decanted liquid, evaporate off the water, and boil for 5 minutes. Cool somewhat, add an equal volume of water, and boil for 3 minutes to remove chlorine. Cool, dilute to 200 ml., add excess of $0 \cdot 1N$ ferrous ammonium sulphate, and titrate back the excess of the latter with standard $0 \cdot 1N$ potassium permanganate, allowing 1 minute for the end point.

Note. 8. The Bureau of Analysed Samples " Ferro-Chromium, No. 203 " (one of the British Chemical Standards) is suitable for this estimation. If a Cr-V steel is used, weigh out accurately about 2 g., and dissolve it directly in 20 to 25 ml. of 60 to 70 per cent perchloric acid. With ferro-chromium, the chromium trioxide initially formed tends to cover the particles of ferro-chromium and thus prevent complete oxidation.

G. Vanadium. The determination of this element is most often required for chromium-vanadium steels : one method will be described. The steel is dissolved and treated exactly as in **F** (*Method 1*) for the estimation of chromium in Cr-V steel until the solution has been titrated with standard $0 \cdot 1N$ potassium permanganate. Then proceed as follows.

Add a moderate excess of $0 \cdot 1N$ ferrous ammonium sulphate (*ca.* 10 ml., but note exact volume) (1) to the cold solution. Then introduce 8 ml. of a freshly-prepared 15 per cent ammonium persulphate solution, and stir for 1 minute to oxidise the excess of ferrous salt (2). Titrate with standard $0 \cdot 1N$ potassium permanganate until a pink colour persists for 1 minute after stirring (3). Calculate the percentage of vanadium in the alloy.

Notes. 1. The excess of ferrous solution reduces the vanadium to the quadrivalent state :

$$2H_3VO_4 + 3H_2SO_4 + 2FeSO_4 = 2(VO)SO_4 + Fe_2(SO_4)_3 + 6H_2O.$$

No changes occur in the valencies of the other elements.

2. The only reaction which occurs in the cool solution in the absence of a soluble silver salt is the quantitative oxidation of the excess of ferrous sulphate solution :

$$2FeSO_4 + (NH_4)_2S_2O_8 = Fe_2(SO_4)_3 + (NH_4)_2SO_4.$$

The net result of the two treatments is the reduction of the vanadium to the quadrivalent state.

3. The reaction is :

$$\begin{aligned}2KMnO_4 + 10(VO)SO_4 + H_2SO_4 + 22H_2O \\ = K_2SO_4 + 2MnSO_4 + 10H_3VO_4 + 8H_2SO_4.\end{aligned}$$

No significant oxidation of chromium or decomposition of persulphate occurs during the short time allowed for the development of the end point with permanganate in the cold solution.

H. Molybdenum. The most satisfactory method for the gravimetric determination of molybdenum in steel is to precipitate the molybdenum with α-benzoinoxime, and ignite the resultant complex to, and weigh it as, molybdic oxide MoO_3 (see Section **IV, 23B**).

Weigh out accurately about 1 g. of the molybdenum steel (1) and dissolve it in 50 ml. of 1 : 6 sulphuric acid : treat the solution with the minimum volume (*ca.* 1 ml.) required to decompose carbides and to oxidise the molybdenum. Boil the solution to expel oxides of nitrogen, and filter the liquid if it is not perfectly clear. Dilute to 100 ml., cool, and heat with sufficient ferrous ammonium sulphate solution to reduce vanadic and chromic acids. Cool to 5° to 10°C, add 10 ml. of the reagent (2 ml. of α-benzoinoxime in 100 ml. of alcohol) with constant stirring, followed by the addition of sufficient bromine water to impart a pale yellow colour to the solution, and finally a few more ml. of the reagent. Allow the mixture to stand for 10 to 15 minutes with occasional stirring, and then filter off the molybdenum complex. Complete the estimation as in Section **IV, 23B** ; use 150 ml. of the special wash liquid. Ignite to constant weight in an electric muffle or crucible furnace at 500° to 525°C. If tungsten is suspected, proceed as described in the *Discussion* to Section **IV, 23B.**

Note. 1. The Bureau of Analysed Samples " Alloy Steel ' B ' " (one of the British Chemical Standards) is suitable for practice in this estimation.

I. Tungsten. Practice in this estimation may be obtained by the use of a chromium-tungsten steel. The tungsten is precipitated as tungstic acid with the aid of hydrochloric and nitric acids, but it is difficult to collect it quantitatively and wash it completely because of the tendency of tungstic acid to form colloidal solutions. This difficulty may be overcome by the addition of cinchonine-hydrochloric acid solution to the suspension (compare Section **IV, 51B**). The precipitate is, however, far from pure ; it contains co-precipitated silica and other substances. The former is removed by volatilisation with sulphuric and hydrofluoric acids, and the amount of the latter (chiefly ferric oxide) is determined by a double fusion with sodium carbonate, the WO_3 forming soluble sodium tungstate.

Weigh out accurately about 1 g. of the steel (1) into a 400 ml. beaker provided with a clock glass cover, add 50 ml. of concentrated hydrochloric acid, and heat until the alloy is decomposed. Remove the beaker from the source of heat, and add *cautiously* 5 to 7 ml. of concentrated nitric acid. Heat to boiling for 5 minutes in order to oxidise all the iron and to convert the tungsten into bright yellow tungstic acid.

Dilute to 100 ml., introduce 5 ml. of cinchonine solution (2), and digest slightly below the boiling point for 30 to 45 minutes, stirring occasionally. The addition of a Whatman accelerator is advantageous. Filter off the precipitated tungstic acid through a Whatman No. 40 or No. 540 filter paper, and wash the precipitate thoroughly with the cinchonine hydrochloride solution diluted 50-fold. Transfer the precipitate and filter to a platinum crucible, dry the paper, char it, and burn off the carbon at the lowest possible temperature. Cool the crucible, add 1 drop of concentrated sulphuric acid and 2 ml. of A.R. hydrofluoric acid. Evaporate off the hydrofluoric acid and expel the sulphuric acid : finally dry at 750° to 850°C in an electric muffle furnace to constant weight (3). The weighed residue will be free from silica, but will consist of impure WO_3 (ferric oxide and other oxides may be present as impurities). Fuse the weighed residue with 5 g. of A.R. anhydrous sodium carbonate, extract the cold melt with 75 to 100 ml. of water, and filter off any insoluble matter on a quantitative filter paper : rinse out the crucible carefully, and wash the paper and residue thoroughly with hot water. Place the filter in the crucible, char the paper, and burn off the carbon ; fuse the residue with 1 g. of A.R. sodium carbonate. Extract the cold melt with 25 ml. of water, filter, and wash the crucible and paper with hot water. Place the filter paper in the crucible, burn, and ignite to constant weight ; this will give the weight of ferric oxide, etc. Deduct this weight from the weight of impure tungstic oxide. Calculate the percentage of tungsten in the alloy.

Notes. 1. Ridsdale's " Alloy Steel, No. 3c " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Alloy Steel, ' W ' " is satisfactory for practice in this determination.

2. Prepared by dissolving 12·5 g. of cinchonine in 100 ml. of 6*N* hydrochloric acid.

3. Alternatively, heat the covered crucible to redness.

J. Titanium. This element may be present in steels up to a few tenths per cent, and is then best determined colorimetrically. Essentially one method consists in adding hydrogen peroxide to a sulphuric acid solution of the steel, and comparing the resultant yellow colour with a standard solution containing known amounts of titanium treated in the same way (compare Section **V, 12**).

Ferro-titanium usually contains 10 to 25 per cent of Ti, and a method for its gravimetric determination will be described.

Weigh out accurately 0·5 to 1 g. of ferro-titanium (1), and dissolve it in 50 ml. of 1 : 4 sulphuric acid in a 600 ml. beaker. When effervescence ceases, evaporate the solution until fumes of sulphur trioxide appear. Cool, add 100 ml. of water, and heat to dissolve iron salts. Filter, and wash the precipitate thoroughly with dilute sulphuric acid ; reserve the filtrate (i). Transfer the filter and precipitate to a weighed platinum crucible, burn off the carbon, then ignite for 10 to 15 minutes, and weigh. Add a few drops of concentrated sulphuric acid and 2 ml. of A.R. hydrofluoric acid, evaporate to dryness, cool, and weigh. The loss in weight is due to SiO_2. Reserve the residue.

Dilute the filtrate (i) to 400 ml., add ammonia solution until a faint precipitate is obtained, then add successively 2 ml. of 1 : 1 hydrochloric acid, 10 ml. of glacial acetic acid, and 10 g. of sodium thiosulphate dissolved in 50 ml. of water. Boil for 10 minutes, allow to settle, filter, and wash several times with 2 per cent acetic acid. Transfer the filter and precipitate to the platinum crucible containing the residue from the silica determination, burn off the carbon, then add 5 g. of A.R. anhydrous sodium carbonate, and fuse until a quiet melt is obtained. Allow to cool, transfer the crucible to a beaker, add 50 ml. of water, and heat until the fused mass is disintegrated and no hard particles remain. Remove the crucible and wash it. Filter and wash well with hot water (2). Dissolve the residue on the paper in 25 ml. of hot 1 : 1 hydrochloric acid, and precipitate in the same way as before by adding ammonia solution, acetic acid and sodium thiosulphate. Filter, wash with 2 per cent acetic acid until free from chloride. Transfer again to a platinum crucible, heat gently at first to burn off the paper and oxidise the carbon, and finally ignite to constant weight. Weigh as TiO_2 (3).

Notes. 1. The Bureau of Analysed Samples " Ferro-Titanium " (one of the British Chemical Standards) is suitable for this estimation.

2. Sodium titanate is insoluble, whilst sodium phosphate and aluminate dissolve.

3. The method of precipitation with tannin and antipyrin (Section **IV, 40B**) is a considerable improvement upon the above procedure. The student should employ this method also, and compare the results obtained. The best method is probably that based upon precipitation with para-hydroxy-phenylarsonic acid (Section **IV, 40D**).

K. Cobalt. This element is present in certain Cr-V-W-Co and Cr-V-W-Co-Mo steels. It may be determined with α-nitroso-β-naphthol or, preferably, with α-nitro-β-naphthol. Both methods will be described.

Method 1. Weigh out sufficient of the steel to contain 0·02 to 0·03 g. of cobalt (1), dissolve it in 20 ml. of 3*N* sulphuric acid, and oxidise the iron by the careful addition of nitric acid, avoiding a large excess. Evaporate to a syrupy consistency, dilute to 200 ml., and slowly add a suspension of zinc oxide until all the iron is precipitated ; avoid a large excess of zinc oxide. Cool, and filter through a dry filter paper. Add 2 ml. of concentrated hydrochloric acid, and evaporate to about 10 ml. Transfer quantitatively with a little water to a 400 ml. beaker, add 10 drops of 100-volume hydrogen peroxide, followed by a slight excess of 2*N* sodium hydroxide to precipitate the cobaltic hydroxide. Dissolve the precipitate in 70 ml. of glacial acetic acid, and dilute to 200 ml. with hot water. Precipitate the cobalt by the addition of freshly-prepared α-nitroso-β-naphthol solution, and heat to boiling. Complete the determination as described in Section **IV, 33A.** Weigh as $Co(C_{10}H_6O_2N)_3,2H_2O$.

Note. 1. For practice in this estimation, the student may employ 0·5 g., accurately weighed, of the Bureau of Analysed Samples " Alloy Steel, ' W ' " (a Cr-V-W-Co steel).

Method 2. Weigh out sufficient of the steel to contain 0·02 to 0·03 g. of Co., and dissolve it in a porcelain dish on the water bath in 10 to 20 ml. of 1 : 1 hydrochloric acid. When the reaction is over, cover with a clock glass, add 1 to 2 ml. of concentrated nitric acid, and evaporate to a syrupy consistency. Moisten the residue with a few drops of hydrochloric acid, and transfer quantitatively with the aid of 200 ml. of water to a 500 to 600 ml. beaker. Heat to boiling, and stir in zinc oxide suspension until the ferric hydroxide coagulates, but avoid a large excess of zinc oxide. Allow to cool, filter through a dry filter paper, and evaporate the filtrate with 1 to 2 ml. of concentrated hydrochloric acid to about 10 ml. Transfer the solution with a little water to a 400 ml. beaker, add 10 drops of 100-volume hydrogen peroxide, and a slight excess of 2*N* sodium hydroxide. Dissolve the precipitated cobaltic hydroxide in 70 ml. of glacial acetic acid, and dilute to 200 ml. with hot water. Precipitate the cobalt by the addition of 30 ml. of α-nitro-β-naphthol reagent, and heat to boiling. Complete the determination as described in Section **IV, 33B.** Weigh as $Co(C_{10}H_6O_3N)_3$.

L. Zirconium. An excellent reagent for the determination of zirconium in steels is *n*-propylarsonic acid (see Section **IV, 41C**). The experimental details for a complex steel, containing 1 to 2 per cent of Zr, will be given.

Dissolve 3 g. of the steel in 40 ml. of concentrated hydrochloric acid and add sufficient concentrated nitric acid to oxidise the iron. Evaporate to dryness, moisten the residue with concentrated hydrochloric acid, evaporate again to dryness, and heat for 30 minutes at 105° to 110°C. Treat the residue with 10 ml. of concentrated hydrochloric acid, and warm gently until solution is complete. Dilute to 100 ml., filter whilst hot, and wash the residue (silica, zirconium phosphate, etc.) well with hot water. Reserve the filtrate (i), and treat the residue as follows in order to recover the small quantity of zirconium present.

Ignite the residue in a platinum crucible, and volatilise the silica with sulphuric and hydrofluoric acids in the usual manner (Section **IV, 70**). Fuse the residue with sodium carbonate, extract with water, filter, and wash well with water. Discard the filtrate. Ignite the residue in a platinum crucible, and fuse with a *little* potassium pyrosulphate. Extract with water containing a few drops of dilute sulphuric acid, filter, and wash with hot water. Add the filtrate and washings to the main filtrate (i).

Dilute the combined filtrates to a volume of 300 ml., heat to boiling, and precipitate the zirconium with 40 to 50 ml. of a 5 per cent aqueous solution of *n*-propylarsonic acid (1). Digest for 30 to 60 minutes, filter whilst hot, with gentle suction, through a quantitative filter paper supported on a filter cone (Whatman, hardened, No. 51), and wash with hot water. Return the filter paper and precipitate to the original beaker, and disintegrate by warming gently with 10 ml. of concentrated hydrochloric acid. Add 100 ml. of water, and reprecipitate the zirconium by adding 10 ml. of the *n*-propylarsonic acid reagent. Digest for 30 minutes, filter as before, and wash well with hot water. Transfer to a weighed porcelain or Main-Smith crucible, ignite gently at first and then more strongly over a Méker type of burner to constant weight. If tin is present, add ammonium iodide, follow the procedure of Section **IV, 22A,** and ignite to constant weight. Weigh as ZrO_2.

Note. 1. This is an approximately saturated solution. The reagent may be purchased from the Eastman Kodak Company, Rochester, N.Y., U.S.A.

M. Copper. This element is usually present to the extent of 0·005 to 1 per cent in certain steels. Two methods will be described for its determination—a gravimetric and a volumetric procedure. The manner of effecting solution of the steel will depend upon whether tungsten is present or absent.

Gravimetric method. (*a*) *Tungsten absent.* Transfer 1 to 10 g., accurately weighed, of the steel (according to the copper content) to a 800 ml. beaker, add 200 ml. of dilute sulphuric acid (1 : 9) and heat gently until solution is complete. (If much chromium or vanadium is present, add a few crystals of potassium chlorate and boil to dissolve carbides.) Dilute to 500 ml. with water, heat to boiling, and saturate with hydrogen sulphide for 30 minutes as the solution cools. Digest for about 30 minutes, add a Whatman accelerator (or one-third of an ashless tablet), filter on a quantitative filter paper, and wash 3 or 4 times with dilute sulphuric acid (1 : 99) which has been saturated with hydrogen sulphide.

(*b*) *Tungsten present.* Dissolve up to 10 g., accurately weighed, of the steel in 100 ml of dilute hydrochloric acid (1 : 1). Add 25 ml. of dilute nitric acid (1 : 1) portionwise, and boil gently until the separated tungstic acid becomes bright yellow. Dilute the solution to 150 ml. with boiling water, digest for 5 minutes, filter the solution (which contains practically all of the copper) and wash with dilute hydrochloric acid (1 : 9). Add 30 ml. of dilute sulphuric acid (1 : 1) to the filtrate, evaporate *just* to fumes of sulphuric acid, cool and add 100 ml. of water. If a small residue to tungstic acid separates, filter and wash with dilute sulphuric acid (1 : 20). To the clear filtrate add 5 g. of tartaric acid, neutralise with ammonia solution, adjust the acidity to 5 per cent by volume of sulphuric acid, heat to boiling and pass a *rapid* stream of hydrogen sulphide for 10 to 15 minutes. Digest the precipitate at 50° to 60°C for 1 hour, filter and wash the precipitate as under (*a*).

Transfer the paper containing the copper sulphide precipitate, which may also contain the sulphides of molybdenum, vanadium, arsenic, tin, etc., to a Main-Smith crucible, ignite at a temperature not exceeding 550°C (1) and fuse with 2 to 4 g. of alkali pyrosulphate. Dissolve the cooled melt in 25 ml. of dilute hydrochloric acid (1 : 9), dilute to 100 ml., neutralise with 5 per cent sodium hydroxide solution and add 0·3 ml. in excess. Boil for 3 minutes, digest for *ca.* 30 minutes, filter and wash the impure copper hydroxide precipitate 5 or 6 times with a cool 0·5 per cent solution of sodium hydroxide. Dissolve the precipitate in dilute hydrochloric acid (1 : 3) or in dilute sulphuric acid (1 : 3), add 3 to 5 g. of tartaric acid, neutralise with ammonia or sodium hydroxide solution, and acidify with dilute acetic acid. Determine the copper with salicylaldoxime as detailed in Section **IV, 19C.**

Note. 1. H. A. Kar (1935) gives the following method. Heat the cooled residue in the crucible with 10 ml. of concentrated hydrochloric acid, transfer the solution quantitatively to a 400 ml. beaker, add 2 to 3 drops of concentrated nitric acid, and then treat with excess of concentrated ammonia solution. Heat to boiling and filter into a 600 ml. beaker ; wash with hot 1 per cent ammonia solution and discard the paper. Dilute the filtrate to 250 ml., heat to boiling, and precipitate the copper by the addition dropwise of a 2 per cent alcoholic solution of α-benzoinoxime (10 to 15 ml.). The subsequent experimental details are similar to those given in Section **IV, 19B** ; the copper is best weighed as $Cu(C_{14}H_{11}O_2N)$ and *not* as CuO as Kar recommends.

Volumetric method. This method yields satisfactory results if the percentage of copper is greater than 0·1. If the steel contains less than 1 per cent of copper, use 5 g. of the sample ; if the copper content exceeds 1 per cent, use 2·5 g. of the steel.

Weigh out accurately about 5 g. of the steel into a 750 ml. conical flask, add 125 ml. of dilute sulphuric acid (1 : 9), and heat until reaction ceases.* Remove from the source of heat, add *ca.* 15 g. of A.R. ammonium persulphate, and boil for 15 minutes. Dilute the solution to 400 ml. with hot water, add 70 ml. of sodium sulphite solution (25 g. of sodium sulphite per 100 ml.) and then 25 ml. of potassium thiocyanate solution (5 g. of potassium thiocyanate per 100 ml.). Boil for 5 minutes, allow to stand for 5 minutes, and filter through a quantitative filter paper. Wash the flask, paper and precipitate with cold dilute sulphuric acid (2 : 98). Transfer the paper and precipitate to a 250 to 300 ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water and 5 ml. of chloroform or carbon tetrachloride. Titrate the copper with standard 0·025M potassium iodate solution as detailed in Section **III, 126.**

IV, 93. ANALYSIS OF AN ALUMINIUM ALLOY

Discussion. There are numerous kinds of aluminium alloys ; thus we have : (i) Ultra-light alloys : these have a moderate aluminium content, a high percentage of magnesium, and small percentage of copper, zinc, silicon, etc.

(ii) Light alloys : these have a high aluminium content, together with small quantities of copper, zinc, magnesium, etc.

(iii) Aluminium-silicon alloys : these may contain up to 20 per cent of silicon, together with small quantities of other elements.

The analysis of a typical alloy of class (ii) will be described.

Procedure. Weigh out accurately about 2 g. of the alloy† and dissolve it in 30 ml. of 20 per cent sodium hydroxide solution, preferably in a Monel beaker (or in a large " nickel " crucible). When the vigorous reaction subsides, heat until solution is complete, dilute with 100 ml. of hot distilled water, filter through a sintered glass crucible, and wash thoroughly with hot water. The residue (*A*) contains the copper, lead, iron, nickel, magnesium, etc., whilst the filtrate and washings (*B*) contain the zinc and aluminium as the zincate and aluminate respectively.

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* For methods of dissolving the steel in the presence of various elements, see *U.S. Steel Corporation, Sampling and Analysis of Carbon and Alloy Steels,* 1938, p. 123 (Reinhold Publishing Co.).

† Ridsdale's " Aluminium Alloy, No. 20 " (one of the Analysed Samples for Students) is suitable for this analysis. The alloy contains *ca.* 87 per cent of aluminium and small quantities of copper, lead, iron, nickel, zinc, and magnesium.

Lead and copper. Dissolve the residue (*A*) in 1 : 1 nitric acid, and determine the lead and copper as in the analysis of German Silver (Nickel Silver) in Section **IV, 89** (**b**) and (**c**) respectively.

Iron. Proceed as in Section **IV, 89** (**d**).

Nickel. Proceed as in Section **IV, 89** (**e**).

Magnesium. Acidify the filtrate from the determination of nickel with concentrated hydrochloric acid and add 5 ml. of the concentrated acid in excess. Then add 25 ml. of concentrated nitric acid, and evaporate on a hot plate in the fume cupboard either to dryness or to fumes of sulphur trioxide if much sulphuric acid is present. This evaporation removes the organic matter, and incidentally also the large amount of ammonium salts present in solution. Dilute the solution to about 200 ml., add 10 g. of ammonium acetate, then an excess of a 2 per cent solution of oxine in 2*N* acetic acid, followed by concentrated ammonia solution until the liquid is strongly alkaline ; stir the mixture vigorously during the addition. Boil the mixture for a few minutes until the precipitate is crystalline, filter it off on a weighed Gooch, sintered glass or porous porcelain crucible, and wash with hot water or, better, with 1 per cent ammonia solution. Dry at 130° to 140°C to constant weight, and weigh as $Mg(C_9H_7ON)_2$. Alternatively, dissolve the washed precipitate in 2*N* hydrochloric acid, and titrate the magnesium with standard potassium bromate solution as in Section **III, 138,** *Procedure B*.

Zinc. Determine the zinc electrolytically in the filtrate and washings (*B*) obtained by solution of the alloy* ; use the method described in Section **IV, 84.**

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* The metallic residue (*A*) may contain a little zinc. If it is desired to recover this, use another sample of the alloy for the determination of zinc. Dissolve the residue (*A*) in a little hot 1 : 1 nitric acid, filter, wash with hot water, render the filtrate and washings alkaline with aqueous sodium hydroxide, boil for 10 minutes, filter off the hydroxides of iron, nickel, etc., and add the filtrate to the main solution (*B*) for the determination of zinc.

Alternatively, acidify the solution (*B*) with dilute sulphuric acid, and determine the zinc volumetrically by titration against standard potassium ferrocyanide solution with diphenylbenzidine as indicator (Section **III, 145**).

Silicon. Dissolve 0·5 g. to 1·0 g., accurately weighed, of the alloy in 15 ml. of 30 per cent sodium hydroxide solution (prepared from the A.R. solid) contained in a covered Monel metal beaker or in a large " nickel " crucible. When the vigorous reaction subsides, evaporate slowly on a hot plate to a volume of about 5 ml. If the solution is dark, add 2 to 3 ml. of 10-volume hydrogen peroxide to accelerate oxidation, and again reduce the volume to 5 ml. Neutralise the concentrated alkaline solution cautiously with 1 : 1 hydrochloric acid, and transfer quantitatively to a Pyrex beaker. Add 20 ml. of 60 to 70 per cent perchloric acid solution (**CAUTION**, see Section **IV, 70**), evaporate to copious fumes, dilute with 50 ml. of hot water, add a Whatman " accelerator " (or one-third of a Whatman ashless tablet), heat to the boiling point, and filter immediately : wash the precipitate with warm 1 per cent hydrochloric acid. Add 10 ml. of 60 to 70 per cent perchloric acid solution to the filtrate, " fume," and filter as before. Dry the filter papers and precipitates at 100°C, transfer to a platinum crucible, and ignite at *ca.* 1000°C. Add a few drops of concentrated sulphuric acid, and ignite to constant weight. Treat the residue with sulphuric and hydrofluoric acids as in Section **IV, 70**, and ignite again to constant weight. The loss in weight will give the silica content of the residue.

IV, 94. ANALYSIS OF A LIMESTONE OR DOLOMITE

Discussion. Limestone consists essentially of calcium carbonate, but it often contains magnesium in amounts which vary from traces to that present in dolomite ; the latter is strictly the equimolecular compound of calcium and magnesium carbonates, $CaCO_3,MgCO_3$. It is of course impossible to differentiate sharply between the various varieties, but it is usual to apply the name dolomite to all carbonate rocks that contain sufficient magnesium carbonate to approximate to the above theoretical composition more or less closely. The procedure to be described is applicable to the analysis of any of the carbonates from $CaCO_3$ to $CaCO_3,MgCO_3$.

The usual minor constituents of limestone or dolomite are iron, aluminium, titanium, manganese, silica (either free or combined as clay or felspar), sulphur (as pyrites FeS_2, or gypsum $CaSO_4$), sodium, potassium, and organic matter. The minerals themselves have many industrial uses, and for judging their suitability for any particular purpose a complete analysis, involving the determination of all the substances just mentioned, is rarely necessary. A shorter analysis will supply all the information that is required. The shorter technical analysis includes the following determinations, all of which are usually made on the same sample :

A. Loss on ignition.

B. Impure silica or insoluble matter.

C. Combined oxides " R_2O_3." This is the residue obtained upon ignition of the precipitate produced by ammonia solution, and consists chiefly of $Al_2O_3 + Fe_2O_3$ together with some TiO_2, Mn_3O_4 and P_2O_5 (chiefly as $AlPO_4$ and $FePO_4$).

D. Calcium oxide.

E. Magnesium oxide.

F. Carbon dioxide (a separate sample is used for this determination).

The experimental details to be described below will not, however, be confined to the determination of the constituents of technical interest ; the mode of estimation of some of the other components will also be indicated.

Attention should be directed to the method sometimes employed for expressing the results of a mineral analysis. It is usual to express the amount of each metal as its oxide, almost always in its higher state of oxidation, and the amount of each anion as the anhydride of the most common acid. Thus magnesium is given in terms of MgO, and phosphorus as percentage of P_2O_5. The fact that the percentage of the constituent is given as the oxide does not, however, imply a determination of oxygen ; rather, the constituent is determined in the customary manner, and the amount present is calculated as if it were the oxide. The method is particularly of value with minerals to which no simple chemical formula can be assigned.

Procedure. **A. Loss on ignition.** Weigh out accurately about 1 g. of the ground, air-dried sample (1) into a weighed covered crucible (porcelain or platinum), and dry at 110°C for 1 hour. Cool and weigh. The loss in weight represents hygroscopic moisture. Then ignite the crucible and its contents slowly (use an electric muffle or crucible furnace at 1000° to 1100°C, or over a Méker type burner). The sample must be heated slowly at first to prevent mechanical loss arising from the sudden evolution of carbon dioxide. Heat for 1 hour at the maximum temperature, cool, and weigh. Repeat the ignition for half-hour periods until the weight of the residue is constant to 0·2 mg. Remember calcium oxide is hygroscopic, and observe the precautions given in Section **IV, 10.** Calculate the percentage loss upon ignition.

Note. 1. Ridsdale's " Dolomite, No. 9b " or " Limestone, Nos. 15b or 15c " (these are Analysed Samples for Students) are suitable for practice in this analysis.

B. Impure silica, or insoluble matter. Transfer the residue after ignition (**A**) to a small covered porcelain dish or casserole, add to the small residue in the crucible a few ml. of 1 : 1 hydrochloric acid, and rinse the solution into the porcelain dish.* Add 5 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid, and stir until the solid has dissolved. Evaporate the solution to dryness on the steam bath or upon a low temperature hot plate at 110° to 120°C ; observe the precautions given in Section **IV, 70A.** Moisten the dry mass with 5 ml. of concentrated hydrochloric acid. warm, and allow to stand for 5 minutes to dissolve basic salts, Add 20 ml. of water, and warm on the steam bath for 10 minutes ; use a glass rod to break up any lumps present. When all the soluble matter has dissolved, filter through a Whatman No. 41 or No. 541 paper. Wash the precipitate thoroughly with 1 : 100 hydrochloric acid, and finally once or twice with water to remove most of the hydrochloric acid. Evaporate the filtrate and washings to dryness in the original porcelain vessel,† heat the residue to 110° to 120°C, then take up in hydrochloric acid and digest as before, using however smaller volumes of hydrochloric acid and water. Filter off the precipitate on a fresh filter, and wash as before. Reserve the combined filtrate and washings (i) for **C.** Place the two silica precipitates in a weighed crucible, dry and ignite at the full temperature of a Méker type burner. Allow to cool and weigh. Calculate the percentage of impure silica or insoluble matter present.

Note. The dehydration is most simply effected by boiling with 12 to 15 ml. of 60 to 70 per cent perchloric acid instead of evaporation to dryness (compare Section **IV, 70,** *Discussion*).

C. Combined oxides. Dilute the filtrate (i) from determination **B** to 200 ml., add 5 g. of ammonium chloride (to prevent precipitation of magnesium hydroxide), heat nearly to boiling, add 2 drops of methyl red indicator, then 1 : 1 ammonia solution until the solution is just alkaline (yellow).‡ Boil for 1 to 3 minutes, filter the precipitate at once, and collect the filtrate in a 600 ml. beaker ; wash the beaker and precipitate twice with hot 2 per cent ammonium chloride solution. Set the filtrate and washings (ii) aside. If the precipitate is small and well washed, reprecipitation can be omitted. If it is large, place the original beaker under the funnel, dissolve the precipitate in a small volume of hot 1 : 1 hydrochloric acid, and wash the paper thoroughly with hot water. Dilute the solution to about 75 ml., add a few drops of methyl red indicator, reprecipitate with ammonia solution as before, add a Whatman accelerator, and filter. Transfer the precipitate completely to the filter, and wash with hot 2 per cent ammonium nitrate solution. Combine the filtrate and washings (ii′) with that of (ii). Place the paper in a crucible, dry and ignite the residue as detailed in Section **IV, 8.** Calculate the percentage of mixed oxides " R_2O_3."

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* Alternatively, weigh out accurately about 1 g. of the powdered mineral into a covered porcelain dish or casserole, and dissolve it in 1 : 1 hydrochloric acid. When effervescence has ceased, evaporate to dryness on the steam bath or low temperature hot plate with stirring by means of a glass rod until the residue is just dry. Continue as in **B.**

† The second evaporation is unnecessary if the silica content is small, and results of only moderate accuracy are required.

‡ If manganese is present or is suspected, add about 5 ml. of bromine water prior to the addition of ammonia solution : the manganese will then precipitate as hydrated manganese oxides.

D. Calcium oxide. Acidify the combined filtrates (ii′) from the ammonia precipitation slightly with dilute hydrochloric acid, and evaporate them to about 250 ml. Add 1 ml. of concentrated hydrochloric acid, and precipitate the calcium by adding slowly to the boiling solution 50 ml. of a hot 4 per cent solution of ammonium oxalate, followed by 1 : 10 ammonia solution until the solution is neutral or slightly alkaline (to methyl red). Test for complete precipitation by adding a little more of the oxalate solution. Allow the precipitate to settle for an hour. Filter off the precipitate, and wash it 2 or 3 times with a cold, 0·1 per cent ammonium oxalate solution. Set aside the filtrate (iii). Place the original beaker under the funnel, dissolve the precipitate in 25 to 50 ml. of hot 1 : 9 hydrochloric acid, and wash the paper with hot water.* Dilute to 100 ml., if necessary, add 5 ml. of the 4 per cent ammonium oxalate solution, boil, then add ammonia solution dropwise until the solution is just alkaline. Allow to stand for 1 hour, filter through a quantitative filter paper, wash the precipitate with a 0·1 per cent ammonium oxalate solution until free from chloride (*ca.* 50 ml.), and once with hot water to remove the excess of oxalate.† Mix the filtrate and washings (iii′) with the previous one (iii), and reserve the liquid (iv). Dry the paper and precipitate, and ignite in a platinum crucible to constant weight. Weigh as calcium oxide, following the procedure of Section **IV, 10.** Calculate the percentage of CaO present.

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* If difficulty is experienced in dissolving the precipitate directly on the filter, wash as much as possible of the precipitate into the original beaker, and dissolve the small amount of the precipitate adhering to the paper by pouring hot 1 : 9 hydrochloric acid repeatedly through the filter. Then add a drop of methyl red, heat until the precipitate has dissolved, adding more dilute hydrochloric acid if necessary.

† If the precipitate is to be weighed as $CaCO_3$ (the better method), filter through a weighed Gooch or porous porcelain crucible, and proceed as in Section **IV, 10.**

E. Magnesium oxide. The combined filtrates (iv) contain excess of oxalate ion and large amounts of ammonium salts; these, as already pointed out (Section **IV, 11**), cause the results for magnesium, when precipitated as magnesium ammonium phosphate, to be high. This error may be avoided by double precipitation or by the removal of the interfering elements. In the latter procedure any silica which may be present is also removed. By oxidation of the hot solution with nitric acid in the presence of chloride ions, oxalate is oxidised to carbon dioxide and water and the ammonium salts principally to nitrous oxide, nitrogen and water. Both methods will be described.

Method 1. Acidify the filtrate (iv) from the determination of calcium, and evaporate to 300 ml. Cool, add a few drops of methyl red indicator, followed by 20 ml. of freshly prepared ammonium phosphate reagent (25 g. of A.R. $(NH_4)_2HPO_4$ in 100 ml. of water). Then add pure concentrated ammonia solution slowly whilst stirring the solution vigorously until the indicator turns yellow; continue the stirring for 5 minutes, keeping the solution alkaline by the addition of more ammonia solution if necessary, and finally add 10 ml. of concentrated ammonia solution in excess. Allow the solution to stand for at least 4 hours, but preferably overnight. Filter off the precipitate and wash it 2 to 3 times with 1 : 20 ammonia solution: discard the filtrate. Place the beaker under the funnel, and dissolve the precipitate in 25 to 50 ml. of hot 1:10 hydrochloric acid. Add 0·1 to 0·2 g. of $(NH_4)_2HPO_4$, and precipitate the magnesium as before in a volume of 150 ml. Allow to stand overnight, filter off the precipitate, and wash it with cold 1 : 20 ammonia solution until free from chloride. Complete the determination as described in Section **IV, 11,** and weigh as magnesium pyrophosphate. Calculate the percentage of MgO present.

Method 2. To the combined filtrates (iv) from the calcium estimation, add 50 ml. of concentrated nitric acid, and evaporate carefully to dryness on a steam bath or upon a low temperature hot plate. Only a small residue (largely magnesium salts) should remain. Add 2 to 3 ml. of concentrated hydrochloric acid and 20 ml. of water, warm the mixture for a few minutes until the solid has dissolved ; if a little silica remains, filter it through a small paper and wash the residue thoroughly. Determine the magnesium in the filtrate as in *Method 1* ; only one precipitation of magnesium ammonium phosphate is necessary in this case. Calculate the percentage of MgO present.

F. Carbon dioxide. Follow the procedure given in Section **IV, 76**, using 0·5 to 0·6 g., accurately weighed, of the sample. Calculate the percentage of carbon dioxide present in the mineral.

Additional determinations. It is sometimes required to estimate the iron content of the original mineral. As a first approximation we may assume that the " combined oxides " are composed of $Fe_2O_3 + Al_2O_3$. This is not strictly true as TiO_2 and P_2O_5 (as metallic phosphates) may be present, but the error introduced by making this assumption is usually small. The Fe_2O_3 may be determined directly as detailed below, and the Al_2O_3 may then be obtained by difference. The Al_2O_3 may be written, if desired, as Al_2O_3 ($+ TiO_2 + P_2O_5$, etc.), if the constituents inside the parentheses are known to be present. Alternatively, the alumina content may be determined directly with 8-hydroxyquinoline (for details, see Section **IV, 95, C1** ; this procedure applies in the presence of titanium).

G. Ferric oxide. The impure silica (**B**) may, and usually does, contain a little of the mixed oxides. Treat the impure silica, contained in a platinum crucible, with 0·5 ml. of concentrated sulphuric acid and 2 to 3 ml. of A.R. hydrofluoric acid, evaporate the whole cautiously, and ignite (see Section **IV, 70A**) ; the loss in weight gives the amount of pure silica present. Fuse the residue with 3 to 4 g. of A.R. anhydrous sodium carbonate, dissolve the melt cautiously in dilute hydrochloric acid, boil, then precipitate with ammonia solution as detailed in **C.** Filter off the precipitate, redissolve it in dilute hydrochloric acid, and again precipitate with ammonia solution. Filter the latter precipitate through a small filter paper, and transfer the paper and precipitate to the original (platinum) crucible containing the " combined oxides," and ignite in the usual manner. It is evident that if only a minute residue is obtained after treatment with sulphuric and hydrofluoric acids, the sodium carbonate fusion is unnecessary except for the most accurate work.

Add 5 to 7 g. of pure anhydrous potassium pyrosulphate to the platinum crucible containing the ignited mixed oxides, and heat *slightly* above the melting point of the pyrosulphate ; keep the crucible covered. After about 20 minutes raise the temperature slowly until eventually the bottom is at low redness and no dark particles are visible (*ca.* 1 hour) : there must be no spattering. Allow the crucible to cool, place it in a 250 to 400 ml. beaker, add 100 ml. of water and 3 ml. of concentrated sulphuric acid, and warm until all the solid has dissolved with the exception of a few flakes of silica. Remove the crucible with a glass rod and wash it thoroughly with water. Filter off the silica on a small filter paper, and collect the filtrate in a 350 ml. conical flask ; wash the paper thoroughly with hot water. Reduce the solution in a Jones reductor (Section **III, 51B**) or with stannous chloride (Section **III, 51A**)* and determine the resultant ferrous iron by titration with standard 0·1*N* potassium permanganate. Calculate the percentage of Fe_2O_3, and by subtracting the weight of the latter from that of the " combined oxides," evaluate the percentage of " Al_2O_3."

H. Alternative procedure for the determination of calcium and magnesium (molybdate method). The procedure given in **D** and **E** involving double precipitation of the calcium as oxalate, followed by double precipitation of the magnesium as the ammonium phosphate is accurate, but time-consuming. The following method is rapid and is based upon the comparative insolubility of calcium molybdate and the solubility of magnesium molybdate under the given experimental conditions.

Heat the neutral solution of calcium and magnesium salts (volume reduced by evaporation to 40 to 50 ml.) to boiling. Add a drop or two of concentrated ammonia solution, followed by the ammonium molybdate reagent (for preparation, see under Cadmium, Section **IV, 18A**) at the rate of 1 drop per second until excess is present. If this rate of addition is exceeded, or if a stirring rod is used, the precipitate adheres very tenaciously to the glass and must be removed with a policeman. (To detect the excess of the molybdate reagent, boil the solution for 10 minutes, allow to settle, and test a drop of the supernatant liquid with a saturated solution of pyrogallol in chloroform ; a brown colouration indicates the presence of molybdate.) When excess of the reagent has been added, boil until the supernatant liquid is perfectly clear (about 15 minutes), and allow to stand until cold (30 to 40 minutes). Filter through a weighed Gooch crucible, containing a thin layer of ground asbestos upon the main pad, wash 10 times with water (100 ml. in all), dry at 130°C for 30 minutes, ignite in a larger crucible (Fig. 2-33) and weigh as $CaMoO_4$. Calculate the percentage of CaO present.

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* If titranium is to be subsequently determined, the hydrogen sulphide method of reduction (Section **III, 51E**) must be used. The methods recommended will yield slightly high results in the presence of titanium, since the reduced titanium will consume a little permanganate solution.

Concentrate the filtrate and washings to about 125 ml., and precipitate the magnesium as magnesium ammonium phosphate in the usual way. Weigh as $Mg_2P_2O_7$, and calculate the percentage of MgO present. The excess of ammonium molybdate present does not interfere.

IV, 95. ANALYSIS OF A FELSPAR*

Discussion. The chief constituents that are normally sought for in an ordinary analysis of a felspar, expressed in petrological nomenclature, are SiO_2 ; Al_2O_3, Fe_2O_3, TiO_2 ; CaO ; MgO ; Na_2O ; K_2O : the loss upon heating to 105° to 110°C is also sometimes determined. Methods for determining all these constituents are given below. The mineral should be in the form of a fine powder (*ca.* 100 mesh). If it is in the form of lumps, the method described in Section **II, 15** employing a hardened steel plate, a percussion mortar and an agate mortar successively may be used. However, for practice in analytical methods, the sample is usually supplied in a finely-divided form suitable for immediate analysis.

Procedure. **A. Solution of the sample.** Weigh out accurately 1 to 1·5 g. of the finely powdered mineral (1) into a platinum crucible (30 ml. size), and, by means of a short thin glass rod, mix it intimately with 6 to 7 g. of A.R. anhydrous sodium carbonate. Remove any powder from the rod by brushing it with a camel's hair brush. Cover the crucible, and heat, at first very carefully over a low Bunsen flame, then gradually over the full Bunsen flame, and finally over the full flame of a Méker type burner until quiet fusion results and decomposition is complete. Take care that the melt does not " boil over." When cold, place the crucible and lid in a covered, deep 7-inch porcelain or platinum basin or in a casserole, cover it with distilled water, and leave overnight, or warm on the water bath until the contents are well disintegrated. When this is the case, add concentrated hydrochloric acid in small portions until an excess is present, and warm on the water bath until the evolution of carbon dioxide ceases. Remove and rinse the cover glass, crucible and lid, and evaporate the contents of the dish or casserole to *complete* dryness on the water bath, crushing all lumps with a glass rod.

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* This is an example of the analysis of an insoluble silicate rock.

Note. 1. Ridsdale's "Felspar (Potash), No. 29" (one of the Analysed Samples for Students) is suitable, but the U.S. Bureau of Standards Sample No. 70 (potash felspar) or No. 99 (soda felspar) is to be preferred since a complete analysis is supplied.

B. Silica. Heat the residue from **A** for an hour at 110° to 120°C to dehydrate the silica, and then complete the determination as in Section **IV, 70B.** At least two evaporations are required to completely dehydrate the silica. Treat the ignited residue with sulphuric and hydrofluoric acids, and determine the SiO_2 by difference. After weighing, set aside the platinum crucible without cleaning.

C. Ferric, aluminium, and titanium oxides. Dilute the filtrate from the precipitation of silica to 200 ml., add 5 g. of ammonium chloride (to prevent precipitation of magnesium hydroxide), then about 3 ml. of bromine water, and boil.* Boil the solution to expel excess of bromine. Add 2 drops of methyl red indicator to the boiling solution followed by pure 1 : 1 ammonia solution until just alkaline; boil for 1 or 2 minutes. Filter off the precipitate at once and collect the filtrate in a 600 ml. beaker; wash the beaker and precipitate with 2 per cent ammonium chloride solution. Set aside the filtrate and washings (i). Place the original beaker under the funnel, dissolve the precipitate in hot 1 : 1 hydrochloric acid, and wash the paper thoroughly with hot water. Dilute the filtrate to 150 ml., reprecipitate by ammonia solution as before, add one Whatman accelerator, and filter. Transfer the precipitate completely to the paper, and wash thoroughly with 2 per cent ammonium nitrate solution. Combine the filtrate and washings (i′) with those of (i). Transfer the precipitate and paper to the platinum crucible containing the residue from the impure silica after treatment with sulphuric and hydrofluoric acids, and ignite the residue as detailed in Section **IV, 8.** Weigh to obtain the weight of $Fe_2O_3 + Al_2O_3 + TiO_2$. The percentage of TiO_2 is usually very small, and, for many purposes, the residue may be regarded as a mixture of $Fe_2O_3 + Al_2O_3$. If time is limited, the percentage of the mixed oxides alone may be returned.

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* This will oxidise iron to the ferric state; it will also precipitate any manganese present as hydrated manganese oxide and thus prevent contamination in the subsequent precipitation of magnesium.

For the determination of the individual elements in the residue, proceed as follows.

C1. Aluminium oxide. Dissolve a portion of the residue, accurately weighed, in sulphuric acid, dilute, and add excess of 10 per cent sodium hydroxide solution. Filter and wash. Acidify the filtrate with hydrochloric acid, and determine the aluminium by the addition of an acetic acid solution of oxine, followed by $2N$ ammonium acetate (for details, see Section **IV, 28B**). Weigh as $Al(C_9H_6ON)_3$. Calculate the percentage of Al_2O_3 present.

C2. Ferric oxide. Use the potassium pyrosulphate fusion method described in Section **IV, 94G** with a known weight of the residue. Reduce with hydrogen sulphide if titanium is subsequently to be estimated. Titrate the ferrous salt with standard $0{\cdot}1N$ potassium permanganate. Calculate the percentage of ferric oxide present.

C3. Titanium oxide. Dissolve a known weight of the mixed oxides in sulphuric acid, and determine the titanium colorimetrically with hydrogen peroxide (Section **V, 12**). If appreciable quantities of titanium are present, precipitate the titanium from the acid solution with tannin and antipyrin (for details, see Section **IV, 40B**), or with para-hydroxyphenylarsonic acid (Section **IV, 40D**), and weigh as TiO_2. Calculate the percentage of titanium oxide present.

D. Calcium oxide. Acidify the combined filtrate and washings (i + i′) from the ammonia precipitation with hydrochloric acid, evaporate to about 150 ml., heat to boiling and precipitate the calcium by means of ammonium oxalate and ammonia solution. Filter. Dissolve the precipitate in dilute hydrochloric acid, and reprecipitate the calcium by the addition of ammonia solution and a little ammonium oxalate solution to the hot solution. Filter and wash with dilute ammonium oxalate solution. Weigh the calcium either as $CaCO_3$ or as CaO. Follow the experimental procedure given in Section **IV, 94D.** Calculate the percentage of CaO present. Reserve all the filtrates and washings (ii).

E. Magnesium oxide. Acidify the combined filtrates and washings (ii) from the determination of calcium, evaporate to 150 ml., and estimate the magnesium by double precipitation with diammonium hydrogen phosphate (Section **IV, 94E**) as the ammonium phosphate. Since the percentage of magnesium is small, precipitation with 8-hydroxyquinoline may be employed with advantage (for details, see Section

IV, 46B and Section **IV, 96E.**) Calculate the percentage of MgO present.

Note. For an alternative and more rapid method for the determination of calcium oxide and of magnesium oxide, see Section **IV, 94H.**

F. Potassium and sodium oxides. *Discussion.* The **J. Lawrence Smith method** (1871) will be described. The very finely-divided sample is decomposed by heating it with its own weight of pure ammonium chloride and eight times its weight of pure calcium carbonate. The sintered mass is leached with water to extract the alkalis and filtered; much of the calcium passes into solution as the hydroxide or chloride, and silica, aluminium, magnesium, iron, etc., remain undissolved. The extract is treated with ammonium carbonate solution to precipitate calcium, and the ammonium salts are removed by volatilisation. The alkali chlorides alone remain, and are weighed. Then sodium or potassium is determined by any of the usual methods in the mixture, and the other alkali is estimated by difference.

Procedure. Weigh out accurately about 0·7 g. of the very finely-divided mineral into an agate mortar, add an equal weight of A.R. ammonium chloride (weighed to the nearest 2 mg.), and grind the two substances together, using a small agate pestle. Weigh out to the nearest decigram 5·6 g. of A.R. calcium carbonate on to a watch glass, and add three-fourths of this, a little at a time, to the mortar and mix thoroughly after each addition. When the mixing is complete, lay the pestle down on the watch glass containing the remainder of the calcium carbonate, and transfer the mixture to a 30 ml. platinum crucible, fitted with a cover, with the aid of a spatula (preferably of platinum): it is advisable to place a little of the calcium carbonate at the bottom of the crucible in order to prevent adhesion of the sintered material at the end of the subsequent ignition. Rinse out the mortar with the remaining calcium carbonate, and transfer to the crucible. The whole operation should be carried out on a sheet of glazed paper, and thus avoid the possibility of any loss in filling the crucible. Cover the crucible with the lid, and tap the crucible gently to cause the powder to settle. Insert the crucible in a hole of a sheet of asbestos (or of "uralite"); about one-third of the crucible should extend below the asbestos. Heat the crucible with a very small flame until the odour of ammonia is no longer perceptible (about 30 minutes—if fumes of ammonium chloride are evolved, the flame should be turned down).

Then heat the crucible over a Bunsen flame for 1 hour, regulating the temperature so that only the lower half of the crucible is at a red heat. Allow to cool, rinse off the cover, add sufficient water to cover the sintered cake, and heat for 10 minutes on the water bath, adding more water if necessary. Wash the contents of the crucible into a dish (porcelain, silica, but, preferably, of platinum) ; crush any lumps present to powder with the agate pestle.

Add enough water to the residue in the dish to give a volume of 50 to 75 ml., and digest on the steam bath for 30 minutes. Filter by decantation through a 9 cm. fast filtering paper into a 600 ml. Pyrex beaker or into a large silica or platinum dish. Add 50 ml. of hot water, heat to boiling, rub the insoluble mass with the pestle for some minutes, and again decant. Repeat the extraction four or more times, depending upon the alkali content of the mineral. Wash the paper with 50 ml. of hot water or, better, with hot, saturated pure calcium hydroxide solution. Test the residue for complete decomposition by warming it with dilute hydrochloric acid ; it should dissolve completely except, possibly, for a few white flocks of silica : no gritty particles should remain.

Treat the filtrate with a few ml. of pure concentrated ammonia solution, and precipitate the calcium present by the addition of excess of ammonium carbonate solution (3 g. of the A.R. salt in 40 ml. of water). Heat the solution to boiling, allow the precipitate to settle, filter, and wash the precipitate with hot water. Redissolve the precipitate in the minimum volume of dilute hydrochloric acid, and reprecipitate with ammonia and ammonium carbonate solutions : this reprecipitation will recover the small amounts of alkali chlorides which may have been coprecipitated. Filter again, and wash with hot water. Combine the filtrates and washings, and evaporate them to complete dryness in a porcelain or silica basin on the steam bath.* Heat the dry residue in the covered basin until all ammonium salts are expelled ; take care to avoid too strong heating. The residue will be dark-coloured, but this does not matter. Dissolve the residue in 25 ml. of hot water, and add, first, a few drops of dilute barium chloride solution to remove traces of sulphate, and, secondly, a few drops of ammonium oxalate solution to precipitate the remaining calcium. Allow to cool, and treat with a few ml. of ammonium carbonate solution in order to remove the excess of barium ; allow to stand overnight.

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* It is better for the subsequent removal of ammonium salts to transfer the solution quantitatively, when it has been reduced to a small volume, to a small platinum dish, and to complete the evaporation in the latter.

Filter off the precipitate through a small paper, evaporate the filtrate to dryness as before, and ignite gently in a covered basin to volatilise the last traces of ammonium salts. Dissolve the residue in water, and filter if necessary. Add 0·5 ml. of concentrated hydrochloric acid to the filtrate, and evaporate to dryness in a small weighed platinum dish or in a large platinum crucible. Heat the dry residue carefully until the chlorides just commence to melt at the edges, then cool for 25 minutes in a desiccator, and weigh as rapidly as possible ; the sodium chloride of the residue is somewhat hygroscopic. Repeat the ignition until constant weight is obtained. This gives the weight of the sodium and potassium chlorides.*

Determine the potassium in the mixed chlorides by the perchlorate method (Section **IV, 48B**), and the sodium by difference. Alternatively, estimate the sodium as sodium magnesium uranyl acetate (Section **IV, 47C**), and the potassium by difference. Calculate the results as percentages of K_2O and Na_2O respectively.

G. Moisture. Dry 1 g., accurately weighed, of the felspar at 105° to 110°C until constant in weight. Calculate the percentage loss in weight.

IV, 96. ANALYSIS OF PORTLAND CEMENT

Discussion. Portland cement is an example of an artificial silicate which is almost completely decomposed by means of acid, thus rendering the process of fusion with sodium carbonate unnecessary. The chief constituents, expressed in technical nomenclature, are : silica, lime, alumina and ferric oxide, magnesia, with small amounts of the oxides of the alkali metals ; sulphuric anhydride and carbonic anhydride. The following constituents are usually determined in an industrial analysis : *A*. insoluble matter ; *B*. silica ; *C*. alumina and ferric oxide ; *D*. lime ; *E*. magnesia ; *F*. Sulphuric anhydride ; *G*. alkalis (by difference) ; *H*. loss upon ignition.

It should be pointed out that the " insoluble matter " may contain metallic elements, and for a complete *scientific* analysis this should be fused with sodium carbonate or with sodium peroxide, and the portion of the melt insoluble in water analysed for the other components. This procedure is, however, unnecessary for technical analysis. Full details for the complete analysis will be evident upon reference to Sections **IV, 94** and **IV, 95.**

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* For work demanding the highest accuracy, the residue should be dissolved in 5 to 10 ml. of hot water, filtered to remove any insoluble material, and the paper washed and ignited in the platinum crucible or dish. The weight of insoluble material, if any, is subtracted from that of the mixed chlorides.

Procedure. **A. Insoluble matter.** Weigh out accurately about 1 g. of the finely-divided portland cement (1) into a 250 ml. porcelain dish or casserole, add 10 ml. of water, followed by 5 ml. of concentrated hydrochloric acid, and cover immediately with a clock glass ; warm until effervescence ceases. Add 40 ml. of water, digest upon a steam bath or upon a low temperature hot plate until the decomposition is complete. Filter off the precipitate, and wash with water. Transfer the filter paper and contents to a Pyrex beaker, and digest at just below the boiling point with 30 ml. of 5 per cent sodium carbonate solution for 15 minutes. Filter, wash with cold water, then with a few drops of 1 : 9 hydrochloric acid, and finally with hot water. Transfer the paper and precipitate to a weighed crucible, burn off the paper, ignite at a red heat, allow to cool, and weigh. Calculate the percentage of insoluble matter.

Note. 1. Ridsdale's " Portland Cement, No. 24 " (one of the Analysed Samples for Students) is satisfactory for practice in this analysis.

B. Silica. Weigh out accurately about 0·5 g. of the sample into a 250 ml. porcelain dish or casserole, add 30 ml. of water, mix with a stirring rod, and then introduce 10 ml. of concentrated hydrochloric acid ; break up any lumps with the stirring rod. Cover the dish, and heat on a water bath until the cement is decomposed. Rinse the clock glass with a little water, and evaporate to dryness on the water bath. The clock glass should be supported on a large glass triangle during the evaporation ; alternatively a Fisher " speedyvap " beaker cover may be used. Complete the determination as in Section **IV, 95B.** Calculate the percentage of silica present.

Note. In a technical analysis the sulphuric-hydrofluoric acid treatment is not usually employed. The residue is heated for 1 hour at 200° to 250°C, then treated with 10 ml. of concentrated hydrochloric acid, warmed gently, diluted with hot water, filtered, and washed until free from chlorides. The filter is dried, and ignited for 1 hour in a muffle furnace, cooled and weighed. The weight of insoluble matter is subtracted from the weight of the residue ; the difference is taken as that of silica. The filtrates are reserved for **C.**

C. " Alumina and ferric oxide." Proceed exactly as in Section **IV, 95C.** The alumina and ferric oxide (and titanium oxide, if present) may be determined as in Section **IV, 95, C1, C2,** and **C3** respectively.

Note. In a technical analysis, the " alumina and ferric oxide " are determined, as is also the ferric oxide. The latter is estimated in a fresh sample of cement as follows. About 1 g. of the cement, accurately weighed, is stirred with 50 ml. of water, 10 ml. of concentrated hydrochloric acid added, and heated to boiling. The ferric iron is reduced with stannous chloride solution in the usual way (Section **III, 51A**), treated with orthophosphoric acid and 2 to 3 drops of diphenylamine indicator, and the ferrous iron titrated with standard potassium dichromate solution (Section **III, 63** and **III, 66**; the other indicators given in the latter Section would be more satisfactory).

D. Lime. Follow the procedure of Section **IV, 95D.**

E. Magnesia. Follow the procedure of Section **IV, 95E.**

The following method based upon **the precipitation of the magnesium as the 8-hydroxy-quinolate** is rapid and accurate. Heat the filtrate and washings from the calcium determination to boiling, add a moderate excess of a 2 per cent solution of oxine in 2*N* acetic acid, followed by 4 ml. of concentrated ammonia solution per 100 ml. of solution ; stir the mixture vigorously during the addition. The supernatant liquid must be yellow at this stage, thus indicating the presence of excess of oxine ; if not, more oxine solution must be added until the yellow colour is obtained. Boil the mixture for several minutes until the precipitate is crystalline, and allow to settle. Filter the precipitate through a weighed sintered glass or porous porcelain crucible, wash it thoroughly with hot water (or, better, with 1 per cent ammonia solution), and dry to constant weight at 130 to 140°C. Weigh as $Mg(C_9H_6ON)_2$. Alternatively the precipitate may be dissolved in 2*N* hydrochloric acid, and the magnesium determined by titration with standard potassium bromate solution as in Section **III, 138,** *Procedure B.*

F. Sulphuric anhydride. Two methods may be used. The first is employed for routine analysis in industry, and takes no account of any sulphur which may be present in the insoluble matter, and is also subject to a number of obvious errors. The second method gives the total sulphur content of the cement, and is therefore to be preferred.

Method 1. Weigh out accurately about 0·5 g. of the cement into a 250 ml. porcelain dish or casserole. Follow the procedure given under *B* to the point where the solution is evaporated to dryness on the water bath. Extract the residue thoroughly with dilute hydrochloric acid, filter, and wash the precipitate. Determine the sulphate in the hydrochloric acid extract by precipitation with barium chloride solution as described in Section **IV, 6.** In order to compute the weight of barium chloride required, you may assume that the cement contains about 3 per cent of SO_3. Express your result as percentage of SO_3.

Method 2. Weigh out accurately about 0·5 g. of the cement into an iron or nickel crucible, add 2 g. each of sodium peroxide and of anhydrous A.R. sodium carbonate, mix thoroughly, insert the crucible in a hole in an asbestos or " uralite " shield (this will protect the contents from the sulphur in the flame gases), and heat the crucible gradually at first with a Bunsen burner, and finally over a Méker burner until the contents of the crucible are in quiet fusion. Allow to cool and, when cold, extract the crucible with hot water in a porcelain dish or casserole. Remove the crucible, and wash it thoroughly, allowing the washings to run into the dish. Cover the dish, and acidify cautiously with hydrochloric acid. Evaporate to dryness on the water bath. Moisten the residue with 5 ml. of 1 : 1 hydrochloric acid, dilute with 200 ml. of water, and filter ; wash thoroughly. Precipitate the sulphate in the boiling solution (300 to 350 ml.) by the addition of barium chloride solution (Section **IV, 6**). Filter, ignite, cool, and weigh. Express your result as percentage of SO_3.

G. Alkalis. Use the J. Lawrence Smith method of Section **IV, 95F.**

Note. In a technical analysis, the alkali content is usually obtained by difference.

H. Loss upon ignition. Weigh out accurately about 1 g. of the cement into a platinum crucible, cover with the lid, and support in a hole in an asbestos or " uralite " board. Heat gradually, and then more strongly with a Méker type burner until constant weight is obtained (about 30 minutes). Allow to cool in a desiccator for 25 minutes before weighing.. Express your result as percentage loss upon ignition.

Note. If desired, the percentage of carbonate present may be determined by the method of Section **IV, 76** ; use 2 to 4 g. for the determination.

CHAPTER V

COLORIMETRIC ANALYSIS

V, 1. General discussion.—The variation of the colour of a system with the change in concentration of some component forms the basis of what the chemist commonly terms **colorimetric analysis.** The colour is usually due to the formation of a coloured compound by the addition of an appropriate reagent or it may be inherent in the desired constituent itself. The intensity of the colour is then compared with that obtained by treating a known amount of the substance in the same manner.

It must however be pointed out that colorimetric analysis is only a special case of the more general **photometric chemical analysis.** The latter may be defined as the analysis which is based upon the measurement of the quantity of light absorbed by a coloured solution (**spectrophotometry, colorimetry**), or by a white suspension (**turbidimetry,** Section **V, 5**), or of the amount of light scattered by a suspension (**nephelometry,** Section **V, 5**). In **colorimetry,** natural or artificial white light is generally used as a light source and determinations are made with a simple instrument termed a **colorimeter.** In **spectrophotometry,** light of a *definite* wave length, extending to the ultra-violet region of the spectrum, constitutes the source of light and this necessitates the use of a more complicated, and consequently more expensive instrument, termed a **spectrophotometer.** If white light is passed through appropriate coloured filters, then light of a definite colour extending over a *narrow range* of wave lengths is obtained. By combining a colorimeter with suitable light filters a **gradation photometer** is obtained. Instruments which may be regarded as belonging to the colorimeter or gradation photometer class are in common use for ordinary analytical work.

The chief advantage of colorimetric methods is that they provide a simple means for rapidly determining minute quantities of substances. With the development of photoelectric instruments (Section **V, 3F**) it is probable that photometric analysis, which is comparatively simple and rapid, may ultimately compete from the point of view of accuracy with volumetric and gravimetric analysis for ordinary (macro) determination of elements and radicals.

Before developing the subject further, the elementary theory of spectrophotometry and colorimetry will be discussed.

V, 2. Theory of spectrophotometry* and colorimetry.—When light falls on a homogeneous layer of a substance it may be reflected, transmitted or absorbed. If the intensity of the incident light of wave length λ is expressed by I_0, that of the absorbed light by I_a, that of the transmitted light by I_t and that of the reflected light by I_r, then :

$$I_0 = I_a + I_t + I_r.$$

For aqueous solutions I_r can usually be neglected by comparison with the other quantities ; furthermore, it is also eliminated by the use of a control, such as a comparison cell, hence :

$$I_0 = I_a + I_t.$$

Lambert (1760) investigated† the relation between I_0 and I_t. Beer (1852) extended the experiments to solutions. Spectrophotometry and colorimetry are based upon Lambert's and Beer's laws.

Lambert's laws. 1. The amount of monochromatic light absorbed by a body is proportional to the intensity of the incident light. This may be expressed in the form that the ratio of the intensities of the transmitted and incident light is constant, *i.e.*,

$$I_t/I_0 = a_t \text{ or } I_t = a_t I_0 \qquad (1).$$

The constant a_t gives the fraction of the incident light which is transmitted by a layer 1 cm. in thickness and is usually termed the *transmission coefficient.*

2. When the thickness of the layer through which the light passes increases in arithmetrical progression, the intensity of the transmitted light decreases in geometrical progression. Thus layers of equal thickness of the same substance absorb the same fraction of the incident light. According to this law :

$$I_t = I_0 a_t^{\,t} \qquad (1'),$$

where t represents the thickness of the absorbing layer.

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* Spectrophotometry proper is mainly concerned with the following regions of the spectrum : ultra-violet, 185–400 mμ (millimicrons) ; visible, 400–760 mμ ; infra-red, 0·76–15μ (microns). In this Chapter our attention will be confined to the visible portion of the spectrum.

$$1\ \text{Å} = 0{\cdot}1\ \text{m}\mu = 10^{-4}\mu = 1 \times 10^{-8}\ \text{cm}.$$

† The first investigation on this subject was carried out by Bouguer (1729), but his work appears to have been overlooked.

If I is the intensity of the incident light of wave length λ, the diminution in intensity of the light on its passage through a small thickness dt of the medium is proportional to I and dt; hence:

$$-dI = k' I\,dt \quad \text{or} \quad -\frac{dI}{dt} = k'\,dt \qquad (2),$$

where k' is a proportionality factor. Integrating (2) and putting I_0 for $t = 0$, we obtain:

$$\log_e \frac{I_0}{I_t} = k' t,$$

or, stated in other terms, $I_t = I_0.e^{-k't}$ (3),

where I_0 is the intensity of the incident light, I_t that of the emergent light, t is the thickness of the absorbing layer in cms., and k' is the *absorption coefficient.* This is the quantitative expression of Lambert's second law; it follows from (3) that each successive layer absorbs an equal fraction of the light. By changing from natural to Briggsian logarithms we obtain:

$$I_t = I_0 \,.\, 10^{-0{\cdot}4343k't} = I_0 \,.\, 10^{-kt} \qquad (4),$$

where k is the *extinction coefficient* of Bunsen and Roscoe (1857). The extinction coefficient is usually defined as the reciprocal of the thickness (t cms.) required to weaken the light to 1/10th of its incident intensity. This follows from (4) since:

$$\frac{I_t}{I_0} = 0{\cdot}1 = 10^{-kt} \text{ or } kt = 1 \text{ and } k = \frac{1}{t}\,.$$

The *extinction* E is given by $E = kt = \log I_0/I_t$.

Beer's law. We have thus far considered the light absorption and the light transmission for monochromatic light as a function of the thickness of the absorbing layer only. In quantitative analysis, however, we are mainly concerned with solutions. Beer (1852) studied the effect of the concentration of the coloured substance in solution upon the light transmission or absorption. Beer found the same relation between transmission and concentration as Lambert had discovered between transmission and thickness of the layer (equation (3)):

$$i.e., \qquad I_t = I_0 \,.\, a_t^{c} \qquad (5),$$

where c denotes the concentration. {When $c = 1$, equation (1) is identical with equation (5)}.

We may write :

$$-dI = k_1' \, I \, dc \qquad (6)$$

in which dc denotes an infinitely small change of concentration. Integrating equation (6) between I_0 and I_t, we obtain as before :

$$I_t = I_0 \, . \, e^{-k_1'c} \qquad (7)$$

and

$$I_t = I_o \, . \, 10^{-0.4343k_1'c}$$
$$= I_o \, . \, 10^{-k_1c} \qquad (8),$$

Combining (4) and (8), we have :

$$I_t = 10^{-\mathbf{k}tc} \text{ (or } \log I_0/I_t = \mathbf{k}tc) \qquad (9) ;$$

this is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer-Lambert law. The value of **k** will clearly depend upon the method of expressing the concentration. If c is stated as molar concentration, **k** is the *molar extinction coefficient.* The latter is equal to the reciprocal value of the thickness in cms. of a 1 molar solution ($c = 1$) at which

$I_t = 0{\cdot}1 \, I_o$, since $I_t = I_o \, . \, 10^{-\mathbf{k}}$ when $t = 1$ and $c = 1$.

Expression (7) holds for varying concentrations of the coloured component if Beer's law is applicable. The latter may be stated in the form that the absorption is proportional to the number of molecules in the light path.

Application of Beer's law. Let us consider the case of two solutions of a coloured substance having concentrations c_1 and c_2. These are placed in an instrument in which the thickness of the layers can be altered and measured easily, and which also allows a comparison of the transmitted light (*e.g.*, a Duboscq colorimeter, Section **V, 4D**). When the two layers have the same colour intensity :

$$\mathrm{I}_{t_1} = I_0 \, . \, 10^{-\mathbf{k}t_1c_1} = I_{t_2} = \mathrm{I}_0 \, . \, 10^{-\mathbf{k}t_2c_2} \qquad (10).$$

Here t_1 and t_2 are the lengths of the columns of the solutions with concentrations c_1 and c_2 respectively when the system is optically balanced. Hence under these conditions and when Beer's law holds :

$$t_1c_1 = t_2c_2 \qquad (11).$$

A colorimeter can therefore be employed in a dual capacity ; (*a*) to investigate the validity of Beer's law by varying c_1 and c_2 and noting whether equation (11) applies, and (*b*) for the determination of an unknown concentration c_2 of a coloured solution by comparison with a solution of known concentration (c_1). It must be emphasised that equation (11) is valid only if Beer's law is obeyed over the concentration range employed and the instrument has no optical defects.

When a gradation photometer or spectrophotometer is used, it is unnecessary to make comparison against solutions of known concentration. With these instruments the intensity of the transmitted light or, better, the ratio I_t/I_0 is found directly at a known thickness t. By changing t and c the validity of the Lambert-Beer law, equation (9), can be tested and the value of $\mathbf{k}$ may be evaluated. When the latter is known, the concentration of an unknown solution c_x can be calculated from the formula :

$$c_x = \frac{\log I_0/I_t}{\mathbf{k}t} \qquad (12).$$

Attention is directed to the fact that the extinction coefficient $\mathbf{k}$ depends upon the wave length of the incident light, the temperature, and the solvent employed. In general, it is best to work with light of a wave length approximating to that for which the solution exhibits a maximum selective absorption ; the maximum sensitivity is thus obtained.

Deviations from Beer's law. Beer's law will generally hold over a wide range of concentration if the structure of the coloured ions or of the coloured non-electrolytes in the dissolved state does not change with the concentration. These include salts such as chromates, permanganates and picrates, and also many organic dyes and coloured substances. Small amounts of electrolytes, which do not react chemically with the coloured components, do not usually affect the light absorption : large amounts of electrolytes may result in a shift of the maximum absorption and may also change the value of the extinction coefficient. If the coloured compound exists in a state of partial dissociation with *two* or more components, the state of dissociation will change with concentration and Beer's law will not be obeyed (*e.g.*, for picric acid). The law also does not apply over any appreciable concentration range for coloured suspensions.

For solutions which do not follow Beer's law, it is best to prepare a calibration curve with solutions of known concentration. Instrument readings, for example, the scale readings on a Duboscq colorimeter, are plotted as ordinates against concentrations in, say, mg. per 100 ml. or 1000 ml. as abscissae. For the most precise work each colour formation should be calibrated throughout the dilution likely to be met with in the actual comparison.

V, 3. Classification of methods of "colour" measurement or comparison.—The basic principle of most colorimetric measurements consists in comparing under well-defined conditions the colour produced by the substance in unknown amount with the same colour produced by a known amount of the material being determined. The quantitative comparison of these two solutions* may in general be carried out by one or more of six methods.

A. Standard series method. The test solution contained in a Nessler tube (Section **V, 4A**) is diluted to a definite volume, thoroughly mixed and its colour compared with a series of standards similarly prepared. The concentration of the unknown is then, of course, equal to that of the known solution whose colour it matches exactly. The accuracy of the method will depend *inter alia* upon the concentration of the standard series ; the probable error is of the order of ± 3 per cent, but may be as high as ± 8 per cent.

For convenience artificial standards, *e.g.*, Lovibond glasses, salt solutions such as ferric chloride in aqueous hydrochloric acid (yellow), aqueous cobalt chloride (pink), aqueous copper sulphate (blue) and aqueous potassium dichromate (orange), are sometimes used. It is essential to standardise the artificial standards against known amounts of the substance being determined, the latter always being treated under exactly similar conditions. The disadvantage of this method is that the spectral absorption curves of the test solutions and of the sub-standard glasses or solutions may be far from identical ; the error due to this cause is greatly magnified in the case of observers suffering from partial colour blindness.

B. Duplication method. A standard solution of the component under determination is added to the reagent until the colour produced matches that of the unknown sample in the *same* volume of solution. This method is less accurate than **A.**

C. Dilution method. The sample and standard solution are contained in glass tubes of the same diameter and are observed *horizontally* through the tubes. The more concentrated solution is diluted until the colours are identical in intensity when observed horizontally through the same thickness of solution. The relative concentrations of the original solutions are then proportional to the heights of the matched solutions in the tubes. This is the least accurate method of all and will not be discussed further.

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* As already pointed out (Section **V, 2**) it is not essential to prepare a series of standards with the gradation photometer or the spectrophotometer, since the concentration of the coloured component in the unknown can be computed from the extinction coefficient, the latter being determined experimentally.

D. Balancing method. This method forms the basis of all colorimeters of the plunger type, e.g., in the Duboscq colorimeter. The comparison is made in two tubes and the height of the liquid in one tube is adjusted so that when both tubes are observed vertically the colour intensities in the tubes are equal. The concentration in one of the tubes being known, that in the other may be calculated from the respective lengths of the two columns of liquid and the relation :

$$c_1 t_1 = c_2 t_2 \text{ (Section } \mathbf{V, 2}).$$

It must be emphasised again that this simple proportionality holds only if Beer's law is applicable, and that the relation holds with greater exactness if a beam of monochromatic light (obtained with the aid of a suitable colour filter) rather than white light is employed. As a general rule it is preferable that the solutions under comparison should not differ greatly in concentration, and for the most accurate work an empirically constructed calibration curve should be used. As usually employed with white light, the accuracy obtainable with a Duboscq colorimeter is of the order of ± 7 per cent ; the accuracy is increased appreciably if monochromatic light (produced with colour filters) is employed.

E. Gradation or step photometer method. This method is essentially a compromise between a spectrophotometric procedure (which employs monochromatic light or light of a very narrow range of wave lengths—*ca.* 50Å) and the colorimeter method (which normally utilises white light). A spectrophotometer is of necessity a very expensive instrument and is also somewhat tedious for analytical usage. Colorimetric methods possess only limited accuracy. By employing a limited range of wave lengths (*ca.* 250Å), secured with suitable light filters, it is possible to construct an instrument which retains the accuracy of the spectrophotometer and the simplicity of manipulation of a colorimeter. Such an instrument is termed a gradation or step photometer and is best exemplified by the Zeiss Pulfrich photometer. With this instrument both the percentage of the incident light intensity which has been allowed to pass through the liquid (i.e., I_t/I_0) and the extinction E (Section **V, 2**) of the solution are directly measured. The extinction coefficient **k** can then be obtained by simply dividing E by the stratum thickness (in cms.). For the measurement of concentration, all that is necessary is to determine for a solution of known concentration c_1 the extinction coefficient $\mathbf{k}_1$ for a suitable light filter. For all subsequent tests with the same filter, if c_2 is the concentration of the unknown solution and $\mathbf{k}_2$ the corresponding extinction coefficient, c_2 is given by the equation :

$$c_2 = c_1 \times \frac{\mathbf{k}_1}{\mathbf{k}_2},$$

which is based upon the validity of the Beer-Lambert law. The latter may be expressed in the form that the concentrations of two solutions are proportional to their extinction coefficients (compare equation (9) in Section **V, 2**). An alternative method of use, which is applicable also when the Beer-Lambert law is not valid, is to carry out a series of determinations in suitable graded solutions of known concentration and to plot a permanent calibration curve ; the filter employed (*i.e.*, the spectral region of the measurements) and the length of the cell must of course be noted. The procedure is rapid and possesses the great advantage that it is unnecessary to prepare fresh standard solutions for each determination.

F. Photo-electric photometer method. In this method the human eye is replaced by a suitable photo-electric cell ; the latter is also employed to afford a direct measure of the light intensity and hence of the absorption. Instruments incorporating photo-electric cells measure the light absorption and not the colour of the substance : for this reason the term " photo-electric colorimeters " is a misnomer ; better names are photo-electric comparators, photometers or, best, absorptiometers.

Essentially most such instruments consist of a light source, a glass cell for the solution, a photo-electric cell to receive the radiation transmitted by the solution and a measuring device to determine the response of the cell. The comparator is first calibrated in terms of a series of solutions of known concentration, and the results plotted in the form of a curve connecting concentration and readings of the measuring device employed. The concentration of the unknown solution is then determined by noting the response of the cell and referring to the calibration curve.

These instruments have been made in a number of different forms incorporating one or two photo-cells. With the one-cell type, the absorption of light by the solution is usually measured directly by determining the current output of the photo-electric cell in relation to the value obtained with the pure solvent. It is of the utmost importance to use a light source of constant intensity—a by-no-means simple problem —and if the cell exhibits a " fatigue effect " it is necessary to allow the photo-cell to attain its equilibrium current after each change of light intensity. The two-cell type of instrument is usually regarded as the more reliable in that any fluctuation of the light source will affect both cells alike if they are matched for their spectral response. Here the two photo-cells illuminated by the same source of light are balanced against each other through a galvanometer ; the test solution is placed before one cell and the pure solvent before the other, and the current output difference measured directly.

Numerous photo-electric comparators are now marketed.* One of the best is the Hilger " Spekker " photo-electric absorptiometer. The latter embodies many novel features, and, like the Pulfrich photometer, makes use of coloured filters for definite ranges of wave lengths (see Section **V, 4F**).

In the following Section it is proposed to discuss the most important of the above methods in somewhat greater detail. For a more complete treatment the reader is referred to the special treatises on the subject (see Appendix, Section **A, 3**).

V, 4. A. Standard series method. In this method colourless glass tubes of uniform cross section and with flat bottoms are usually employed. These are termed **Nessler tubes.** The best variety has a polished flat bottom.† They are made in either the " low " form with a height of 175 to 200 mm. and a diameter of 25 to 32 mm. (Fig. 5-1) or as a " high " form with a height of 300 to 375 mm. and a diameter of 21 to 24 mm. The solution of the substance being determined is made up to a definite volume, and

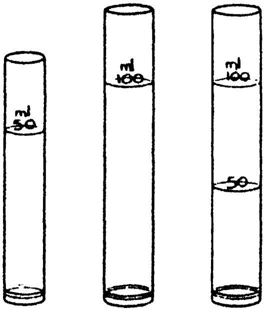

Fig. 5-1.

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* For example : " Photoelectric Turbidimeter and Colorimeter " (Baird and Tatlock (London) Ltd., London, E.C.2, England) ; " Electrophotometer " (Fisher Scientific Co., Pittsburgh, Pa., U.S.A.) ; " Photelometer " (Central Scientific Co., Chicago, U.S.A.) ; " Photoelectric Colorimeter and Turbidimeter " (Eimer and Amend, New York, U.S.A.).

† The " double plane " Nessler tubes supplied by the Fisher Scientific Co. of Pittsburgh, U.S.A. have bottoms which have been ground and polished optically plane on both sides and then fused to the tubes. They are very satisfactory in use, since they produce a uniform field of colour intensity.

the colour is compared with that of a series of standards prepared in the same way from known amounts of the component being determined. Fifty or 100 ml. of the unknown and standard solutions are placed in Nessler tubes, and the solutions are viewed *vertically* through the length of the columns of the liquid. The concentration of the unknown is equal to that of the standard having the same colour.* As a general rule it will be found that the colour intensity of the unknown lies between two successive standards. Another series of standards may then be prepared covering the latter range over smaller concentration intervals. Thus, for example, in the determination of a particular constituent the first series of standards might cover the range 0·1, 0·2, 0·4, 0·6, 0·8 and 1·0 mg. per litre, and it is found that the colour of the unknown lies between 0·4 and 0·6 mg. per litre. The second series of standards may then be prepared containing 0·40, 0·45, 0·50, 0·55 and 0·60 mg. per litre. Further comparison may then show that the value lies between 0·45 and 0·50 mg. per litre, and for many purposes this should be returned as 0·48 mg. per litre. If a more accurate value is required, and provided the colour intensity of the solution and also the apparatus employed will permit of finer comparison, another series of standards covering the range of, say, 0·45, 0·475 and 0·50 mg. per litre may be made up and the unknown compared with these standards.

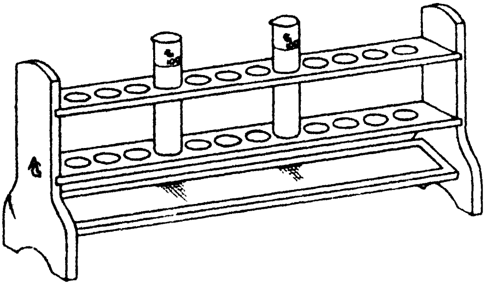

FIG. 5-2.

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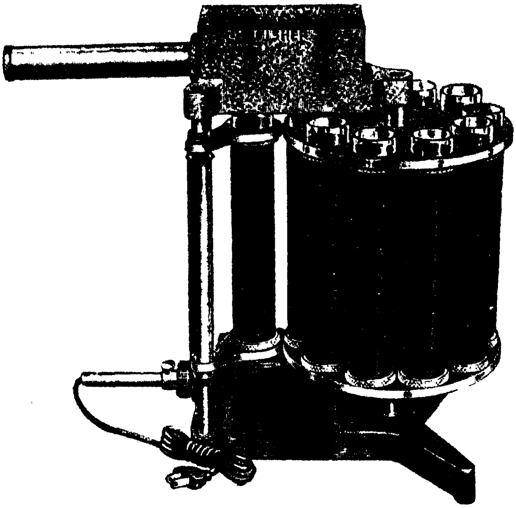
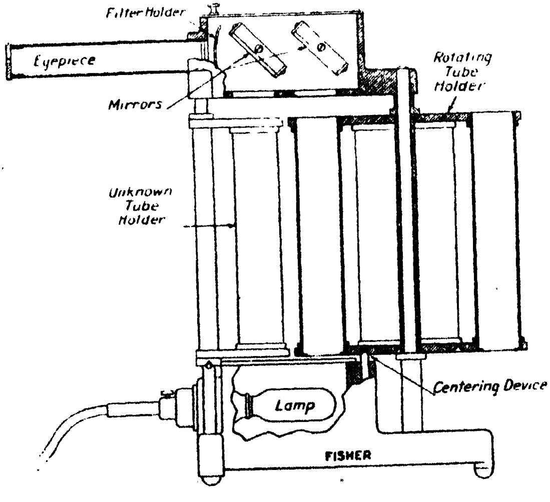
* It is advisable wherever possible to make a preliminary determination of the strength of the unknown solution by adding from a burette a solution of the component in known concentration to a Nessler tube containing the reagents diluted with a suitable amount of water until the depth of colour obtained is practically the same as that of an equal volume of the unknown solution also contained in a Nessler cylinder and standing at its side. A series of standards on either side of this concentration is then prepared.

For the comparison of colours in Nessler tubes, the simplest apparatus consists of a modified test-tube rack (Fig. 5-2). It is constructed of wood, finished dull black, and is provided



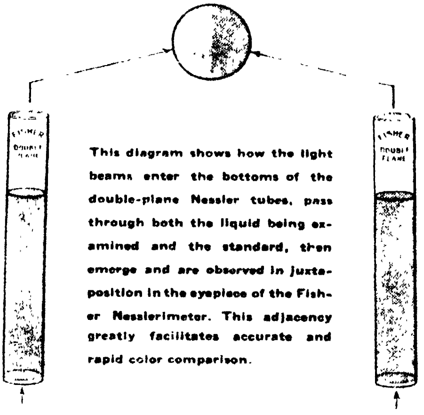
(*a*)

Fig. 5-3.



(*b*)

Fig. 5-3.



This diagram shows how the light beams enter the bottoms of the double-plane Nessler tubes, pass through both the liquid being examined and the standard, then emerge and are observed in juxtaposition in the eyepiece of the Fisher Nesslerimeter. This adjacency greatly facilitates accurate and rapid color comparison.

(*c*)

Fig. 5-3.

with an inclined opal-glass reflector. The Nessler tubes rest on a narrow edge and do not come into contact with the reflector. A more satisfactory method is to employ the Fisher "**Nesslerimeter.**" The apparatus itself is shown in Fig. 5-3 (*a*) and the optical arrangements (*c*) in Fig. 5-3 (*b*).* It consists of a substantial cast base with a housing containing a 15-watt daylight blue lamp for illuminating with equal intensity both tubes being compared. There is a rotating support, accurately mounted, which has holders for 10 Nessler tubes to contain the graded standard solutions. The support for the Nessler tube containing the unknown sample swings in and out of position so that it can be easily inserted or removed. The light emerging from the two Nessler tubes containing the standard solution and the unknown passes into a light-tight housing at the top of the instrument where the two beams encounter a mirror and lens system which brings them side by side in the eyepiece (see Fig. 5-3 (*c*)). A special filter holder is also provided for the insertion of colour (*e.g.*, Wratten or Corning or Jena) filters. Comparison can thus be rapidly made of the colour of the unknown solution with that of any one of 10 standards, previously prepared.

There are a number of apparatus which employ permanent glass colour standards ; these are usually prepared from

* These diagrams are reproduced by the courtesy of the Fisher Scientific Co., of Pittsburgh, Pa., U.S.A.

Lovibond or similar type glasses. An inexpensive model is shown in Fig. 5-4 (Plate II). This is the **B.D.H. Lovibond nesslerimeter.*** It consists essentially of a bakelite case for holding vertically two Nessler glasses between a reflector and a detachable rotating disc having 9 apertures containing a series of graded permanent glass colour standards. Each disc contains a series of standards designed for one particular test conducted under specified conditions. Discs are available for many of the common determinations by colorimetric methods, and the manufacturers are continually extending the range. The discs at present available include : ammonia (with Nessler's reagent) ; bismuth (with potassium iodide) ; copper (with dithio-oxamide) ; iron (with thioglycollic acid) ; lead (with sodium sulphide) ; chlorine (with *o*-tolidine) ; nitrate (with 2 : 4-xylen-1-ol) ; silicate (with ammonium molybdate) ; *p*H 5·2 to 6·8 (with bromo-cresol purple) ; *p*H 6·0 to 7·6 (with bromo-thymol blue) ; *p*H 6·8 to 8·4 (with phenol red) ; *p*H 7·2 to 8·8 (with cresol red) ; *p*H 8·0 to 9·6 (with thymol blue) ; and *p*H 9·0 to 11·0 (with B.D.H. ' 9011 ' indicator). The instrument can of course be employed as a simple comparative colorimeter as described above ; the colour disc is then removed.

B. Duplication method. This method finds its chief application in the so-called **colorimetric titration.** A known volume, say 50 or 100 ml., of the solution is placed in a Nessler cylinder (Fig. 5-1) and a measured volume of the reagent or reagents is then added. An equal volume of water (50 or 100 ml.) together with the same volume of the reagent is introduced into another similar Nessler cylinder. For mixing the solutions both cylinders are provided either with a glass tube on which a flattened bulb (*ca.* 1 cm. diameter) is blown or with a stirring rod of which the lower end is flattened to a width of 1 cm. and over a length of several cms. The tubes should also be provided with black or brown paper cylinders to exclude light from the sides. The colour intensities are compared by holding the tubes close together over a white surface, such as sheet of opal glass or, better, in a Nessler tube stand (Fig. 5-2). A solution containing a known concentration of the constituent being determined is added to the blank solution from a burette (preferably of the micro type)

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* The apparatus is manufactured by The Tintometer Ltd., Milford, Salisbury, in association with The British Drug Houses Ltd., Graham Street, London, N.1, England ; it is reproduced by courtesy of the former company. A similar apparatus is marketed by F. Hellige and Co.

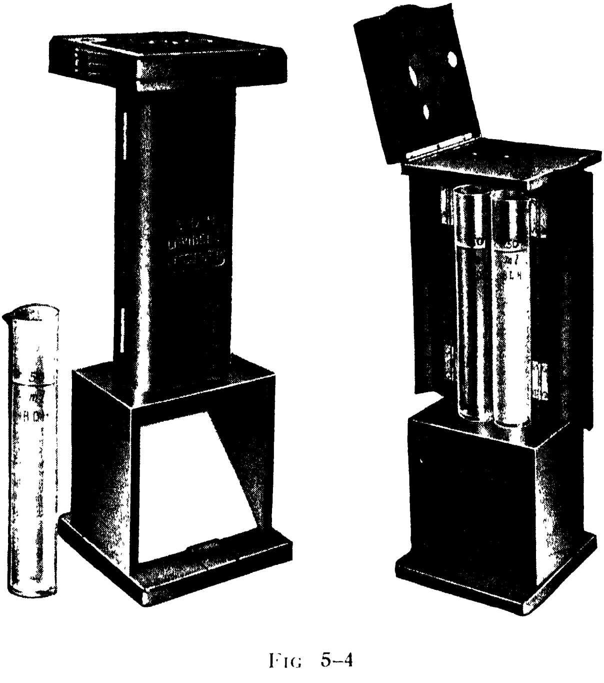

FIG 5–4

until the colours of the two solutions viewed by looking down into the tubes match. As a rule, if the volume of the standard solution required to match the colour of the unknown is less than about 2 per cent of the total volume, the volume change due to the addition of the reagent may be neglected. It may, however, be allowed for by a simple calculation, or the estimation may be repeated by taking 100 $-x$ (or 50 $-x$) ml. of water, where x is the volume of the standard solution employed in the first titration. Several determinations should be carried out and the positions of the tubes should be interchanged—thus that on the right-hand side should be put to the left of the observer and *vice versa.*

It must be emphasised that this method can only be applied when the colour is independent of the mode of mixing, for in one tube a very dilute solution of the substance to be determined is mixed with the reagent, whilst in the other tube a comparatively concentrated solution of the substance is mixed with a dilute solution of the reagent. The development of colour should be practically instantaneous and remain permanent during the time required for the measurements; foreign substances present in the unknown should not affect the colour. The method is, at best, only an approximate one, but has the advantage that only the simplest apparatus is required.

D. Balancing method. Plunger-type colorimeters. The plunger-type of colorimeter with the two halves of the field of view illuminated by the light passing through the unknown and standard solutions respectively was invented by J. Duboscq of Paris in 1854; various improved modifications of the instrument have been subsequently developed by manufacturers of optical apparatus. One of the best of these is the Bausch and Lomb model. Before describing the latter, reference must be made to **Hehner cylinders** (Fig. 5-5). These are utilised in pairs, and are the simplest form of apparatus

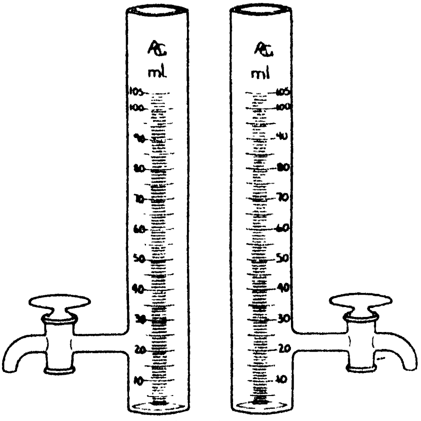

FIG. 5-5.

employed in matching colours by the balancing method. Each cylinder has a glass stop-cock about 2·5 cm. from the bottom through which liquid may be drawn off until the colour in the two cylinders is the same in intensity when viewed vertically. The cylinders are graduated at 1 ml. intervals and usually have a capacity of 100 ml. : they should have flat, carefully ground and polished bottoms of clear glass and be uniform in bore. It is advisable to place them in a box so arranged that the light is reflected from the bottom of the latter up through the tubes.

A **Duboscq colorimeter** (Bausch and Lomb, 40 mm. " biological " model[*]) is shown in Fig. 5-6 (Plate III) and a sectional diagram in Fig. 5-7 (Plate III). The essential principles of the instrument will be evident from Fig. 5-8. Light from an even source of illumination (*e.g.*, from the special mirror **A**, adjustable on a horizontal axis) is passed through the two sides of the instrument. There are interposed in these two light paths the solutions to be tested contained in two movable cups **B** and **B′** ; some of the light in passing through the liquids is absorbed, the amount of absorption depending upon the depth and the concentration of the solution. The two beams of light are now brought to a common axis by means of the rhombohedral prisms **E**. Light from one cup illuminates one half of a circular field and light from the other cup illuminates the other half. The observing microscope **F** at the upper end of the instrument, by which the observer sees both fields with one eye, is focussed on the line of separation of the two fields. When the eye piece is properly focussed, the observer sees the field of view divided into two semi-circular half-fields separated by a fine line and can thus be compared with ease and accuracy. It is important that the illumination should be identical on both sides ; the mirror surface **A** must be per-

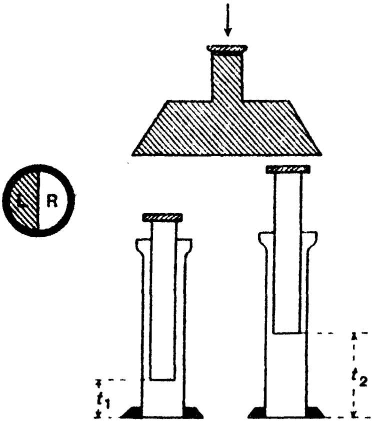

FIG. 5-8.

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[*] The block of Fig. 5-6, and also details concerning the use of the instrument, are reproduced by courtesy of the Bausch and Lomb Optical Co. of Africa House, Kingsway, London, W.C.2, England, and of Rochester, N.Y., U.S.A.

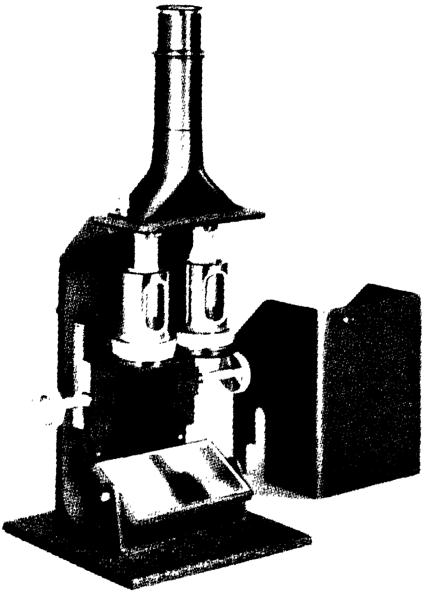

FIG. 5–6

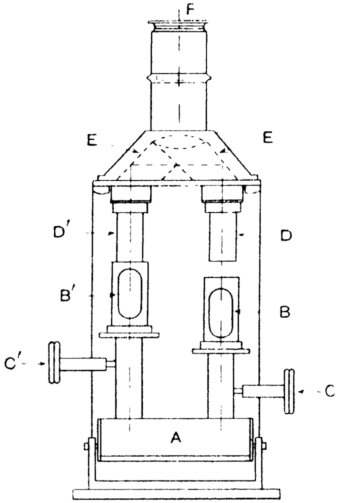

FIG. 5–7

fectly clean. It is now possible to alter the depths of the two columns of liquid until the two halves of the field are identical in intensity. When this condition holds and Beer's law is applicable, the concentrations of the two solutions are inversely proportional to their depths, which are read on the scales of the instrument.

The all-glass cups are made of optical glass in two pieces ; the discs which form the bottoms have ground and polished surfaces and are fused to the cylinders. The cups, which serve to receive the solutions, are mounted movably on slides ; the cups may be raised or lowered by turning the milled heads **C** and **C′**, each of which actuates a rack and pinion. Two solid glass plungers **D** and **D′** of optical glass, matched for colour and having optically plane ends, are attached to the frame of the instrument by means of metal adaptors in which they are firmly cemented ; they are located in a fixed position on the axis of the instrument which passes through the centres of the cups. Stops are provided which prevent the cups and plungers being brought violently together. The scales and verniers (not shown in Fig. 5-7 (Plate III), but one is visible in Fig. 5-6 (Plate III) can be read to 0·1 mm. ; they measure the distance between the bottom of the cup and the plunger.

Use of Duboscq colorimeter. The following details apply to the Bausch and Lomb model, but can be adapted, with only slight modification, to any make of Duboscq colorimeter.

Before the liquids are introduced into the cups, the instrument must be adjusted for even illumination. If sky-light is to be used, an unobstructed north window should be chosen and the colorimeter placed directly in front of it. While looking into the eyepiece, turn the mirror so that the maximum illumination is obtained. The best way to do this, for daylight, is as follows. Prepare a dilute solution of a coloured inorganic salt, such as potassium permanganate. Place equal volumes of the solution in each cup, using sufficient to about half-fill each cup. Set one of the cups at 15 to 20 mm. depth and take a series of readings with the other cup. If the average is not the same as the setting for the first cup (within 0·1 to 0·2 mm.), change the position of the colorimeter with reference to the illumination and repeat until a position is found when the right and left readings are the same. The position of the mirror and colorimeter must not be changed from this point onwards.

The most satisfactory results are obtained, however, not with daylight which may vary both in intensity and in colour quality and may also be influenced by moving large objects in the vicinity of the colorimeter, but with a lamp designed for colorimetric work. The adjustment for illumination is similar to that given above, except that the lamp or mirror is adjusted instead of shifting the colorimeter. There is also a special Bausch and Lomb colorimeter lamp available, provided with filters, etc., which requires no adjustment.

Make sure that the readings are zero when the plungers touch the bottom of the cups. Place the standard solution in one cup and an equal volume of the unknown solution in the other. Set the standard at a scale reading of 15 to 20 mm. Then adjust the unknown until the fields are matched. Take the readings on both scales. Carry out 6 to 10 adjustments with the cup containing the unknown solution, and calculate the mean value. If t_1 and t_2 are the average readings for the cups containing the solutions of known and unknown concentration respectively, and c_1 and c_2 are the corresponding concentrations, then if Beer's law holds :

$$c_1 t_1 = c_2 t_2 \quad \text{or} \quad c_2 = c_1 \frac{t_1}{t_2}.$$

Frequently, owing to optical and mechanical imperfections of many colorimeters, the same reading cannot be obtained in the adjustment for illumination when the cups are filled with the same solution and balanced. In such a case one of the cups (say, the left one) is filled with a reference solution (which may be a solution containing the component to be determined) of the same colour and approximately the same intensity as the unknown and the plunger set at some convenient point (about the middle) of the scale. Fill the other cup with a solution having a colour corresponding to a known concentration of the component to be determined, and adjust this cup to colour balance. Take the reading and repeat the adjustment, say, 10 times in such a way that the balancing point is approached 5 times from the lower and 5 times from the higher side. Calculate the average reading (t_1). Remove the cup, rinse it thoroughly and fill it with the unknown solution. Repeat the balancing exactly as for the standard solution, and find the average of, say, 10 readings (t_2). If c_1 is the concentration in the standard solution, then the concentration of the unknown solution is given by:

$$c_2 = c_1 \frac{t_1}{t_2}.$$

(This method is comparable in many respects to the method of weighing by substitution—see Section **II, 6C.**) If Beer's law is not valid for the solution, it is best to arrange matters so that the colour intensity of the standard lies closely to that of the unknown.

Suggestions as to general maintenance of the colorimeter.*

1. Keep all cups and plungers scrupulously clean.
2. Before using the colorimeter be sure that it is carefully adjusted for even illumination, and do not subsequently change the position of the instrument while in use.
3. Be sure that the verniers are adjusted to zero before using.
4. Wash the mirror or milk glass reflector occasionally so that it may reflect light evenly.
5. Rinse off the plungers before putting away the instrument to avoid contamination of other solutions.
6. Do not fill the cups to such a depth that they will overflow when the plunger is brought into contact with the cup bottom.

E. Gradation or step photometer method. The Zeiss Pulfrich photometer† mounted on an optical bench is shown in Fig. 5-10, while Fig. 5-9 gives a diagrammatic section through the apparatus. The optical system consists of two parallel telescopes having a common eyepiece, and there is an arrangement by means of which a number of different colour filters

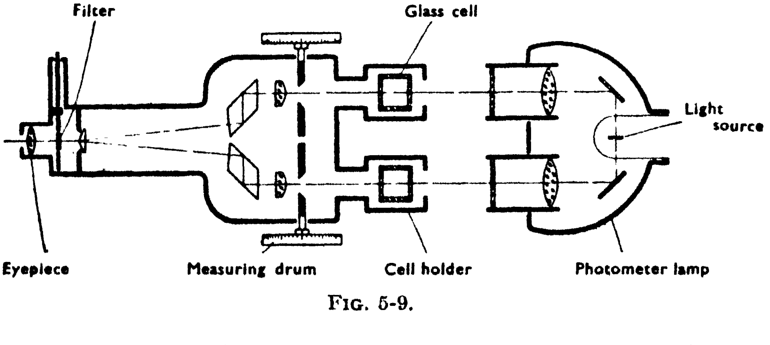

FIG. 5-9.

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* Reproduced, with permission, from " Directions for Use " issued with the Bausch and Lomb colorimeters.

† Figs. 5-9 and 5-10 and some of the descriptive matter are reproduced by the courtesy of Carl Zeiss (London) Ltd., 37–41 Mortimer Street, London, W.1, England.

may be introduced into the path of the light. The field of view is divided by a vertical separating line into two semicircular portions, corresponding to the photometer apertures.

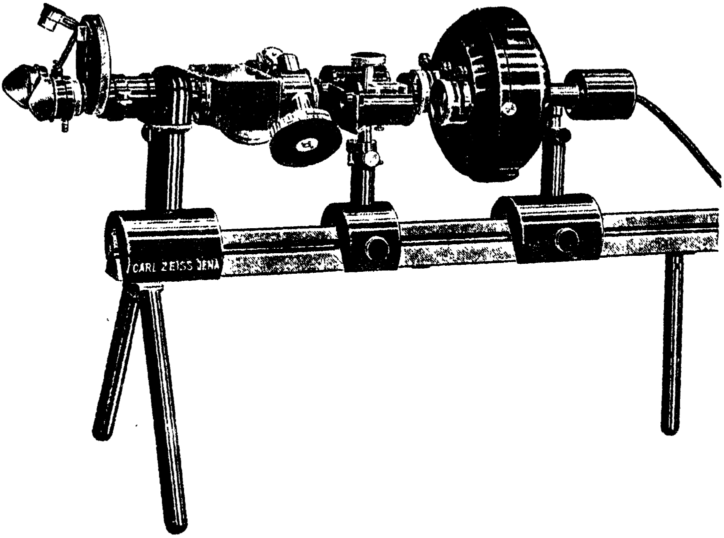
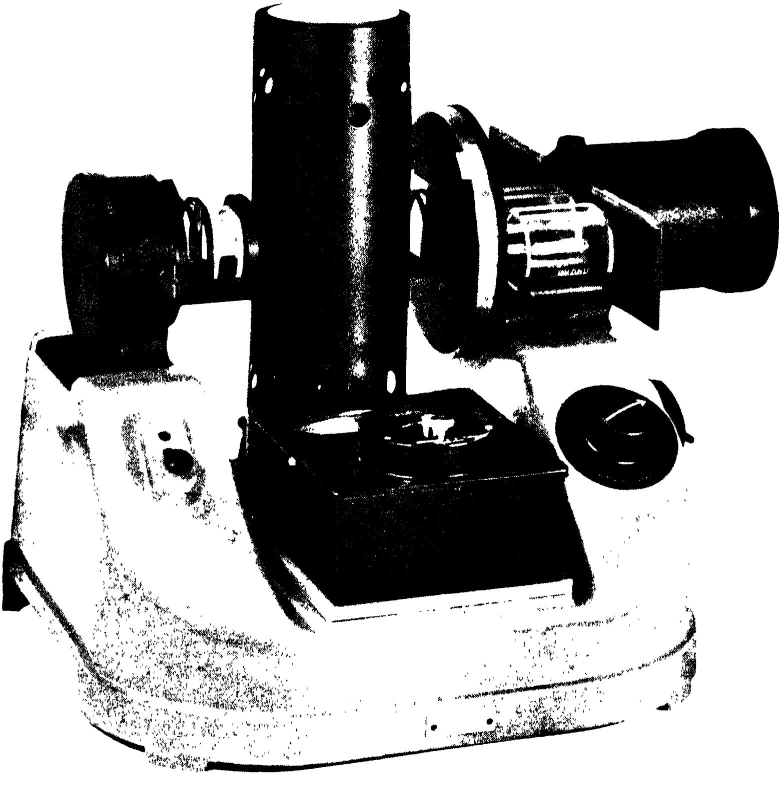


FIG. 5-10.

The measuring device consists of two micrometer drumheads mounted on the openings of the telescopes (photometer diaphragms) ; by turning the drums the intensity of each half of the field can be varied by measurable amounts. The drums are graduated so as to permit approximately the same percentage accuracy for intensely and feebly absorbent fluids. The concentration of a coloured solution and the absorption of monochromatic light are connected by the Lambert-Beer law (Section **V, 2**), thus permitting the determination of the concentration from the light absorption. Nine selective (" *S* ") light filters are employed to cover limited portions of the visible spectrum. Illumination is provided by means of a special photometer lamp with an L-bulb which yields the very intense illumination required for use with the " *S* " filters. For truly monochromatic light a " Hagephot " mercury vapour lamp is available ; this is provided with 3 filters for the yellow, green and blue mercury lines.

Use of Zeiss Pulfrich photometer. A cell of suitable stratum length (10 to 250 mm.) is filled with the unknown solution and placed in one of the cell holders, say, the left. An identical



Adam Hilger, Ltd., London

FIG 5–12

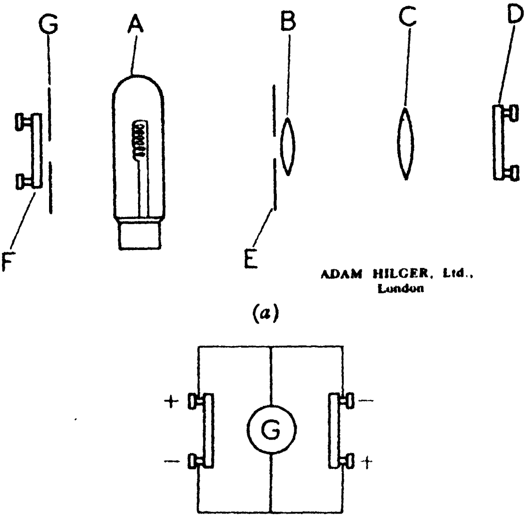
cell is then filled with distilled water, and placed in the other cell holder. The light-filter holder is then rotated, thereby introducing various filters successively into the path of the light, until the colour difference vanishes. Thus with a yellow solution, a blue filter is introduced and the field of view appears blue on both sides but different in intensity. By turning the drum on the right, the intensity on the left side of the field is varied until both halves of the field of view appear equally bright ; the reading on the drum will then give directly the diminution which the coloured light has experienced in passing through the unknown liquid. The reading on the outer (black) scale of the drum gives the intensity of the transmitted light expressed as percentage of the incident light (*i.e.*, I_t/I_0), and the reading on the inner (red) scale gives the extinction E of the test solution. If E ($= \mathbf{k}t$) is divided by the stratum thickness (in cms.) the extinction coefficient $\mathbf{k}$ is obtained. If c_1 and $\mathbf{k}_1$ are the concentration and extinction coefficient respectively for a solution of known concentration, c_2 and $\mathbf{k}_2$ the corresponding values for an unknown solution, then, provided the Beer-Lambert law is valid,

$$c_2 = c_1 \frac{\mathbf{k}_2}{\mathbf{k}_1}.$$

It is usually convenient to prepare a permanent calibration curve (see Section **V, 3E**).

F. Photo-electric photometer method. This method is well exemplified by the "**Spekker**" **photo-electric absorptiometer.** The optical arrangements are shown in Fig. 5-11 (*a*), and the photo-electric circuit in Fig. 5-11 (*b*). Fig. 5-12 (Plate IV) is a photograph of the instrument. A 100-watt projection lamp **A,** mounted in a cylindrical lamphouse and run from the electric mains supply, is the source of light. A lens **B** mounted in the housing to the right of the lamp forms a parallel beam of light ; the beam passes on through the cell containing the solution and then falls on another lens **C** which forms an image of the lamp filament on a photo-electric cell **D** (termed the "indicating cell"). A calibrated variable aperture **E** is mounted immediately in front of the lens system, and enables the intensity of the light falling on the photo-cell to be varied by known amounts. Since there is an image of the filaments on the cell, there is no change in the photo-cell area illuminated when the aperture alters : only the quantity of light reaching the cell is controlled by the variable aperture

The scale associated with the aperture is so calibrated that, if R is the reading corresponding to a degree of opening such that the amount of light transmitted is $1/a$ of that admitted when the aperture is fully open, then $R = \log a$. This function (known as density) was chosen because it is approximately linear with the concentration of a solution, over small ranges.



ADAM HILGER, Ltd., London

(*a*)

(*b*)

FIG. 5-11.

Light from the lamp also falls on the photo-cell **F**, termed the " compensating cell," mounted in the housing to the left of the lamp. The amount of light falling on this photocell (which is protected by a 1 cm. water cell) can be varied by means of an iris diaphragm **G** mounted in front of it. The two photo-cells are connected in opposition across a galvanometer so that, when the photo-electric currents given by the cells are equal, the galvanometer shows zero deflection.

Use of " Spekker " photo-electric absorptiometer.* This is best illustrated by describing the procedure for making a determination. Let us suppose that it is desired to compare the depth of colour or, more precisely stated, the amount of light absorbed by two liquids s_1 and s_2, the latter being the more deeply coloured, i.e., the more absorbing.

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* The diagrams and descriptive matter are reproduced by courtesy of the sole manufacturers: Messrs. Adam Hilger Ltd., 98 Kings Road, London, N.W.1, England.

1. Place s_2, contained in the special cell, into the beam, and open the variable aperture to its full extent by setting the drum at zero.

2. Adjust the *iris diaphragm* in front of the compensation cell until the galvanometer shows zero deflection.

3. Substitute s_1 for s_2 when the galvanometer will be seen to be deflected.

4. Adjust the *calibrated variable aperture* by means of the drum until the galvanometer returns to zero, and take the reading on the drum.

This series of operations takes less than half a minute. The cells containing the liquids are mounted side by side, and are easily interchanged by pushing the slide along an inch or so until it clicks into the correct position.

If we assume that the light intensity remains constant throughout the series of operations, then the current given by the indicating cell at the end of operation *4* is the same as at the end of operation *2* (since in each case it balances the output of the compensating cell). The difference in the illumination condition in the two cases is that in the second case the intensity-reduction produced by closing down the aperture is substituted for the reduction produced by the absorption of the specimen. The ratio of the area of the partly closed aperture to that of the aperture when fully open is thus a measure of the absorption of the liquid. Since both photocells are affected alike by changes in the intensity of the lamp, the reading is unaffected by changes occurring during the series of operations.

The sensitivity of the instrument in detecting small differences between the absorption of two liquids is greatly increased by the use of a suitable light filter, the filter being such that the range of wave lengths over which it transmits includes only the range of wave lengths over which the solution absorbs. The use of a filter also, usually, simplifies the relation between the readings on the instrument and the concentration of the solution. A set of 5 pairs of filters is supplied with the instrument. The all-glass cells are made of Pyrex glass and are either 1 cm. or 4 cm. in length ; the latter are employed for feebly coloured solutions.

It should be noted that the photo-electric cells under prolonged illumination with red light tend to behave irregularly. For this reason it is best, as a general rule, only to switch on the instrument immediately before the start of a series of readings and to switch it off immediately when finished. This precaution is really only necessary when using red or yellow filters.

For the routine use of the absorptiometer in colorimetric determinations, it is necessary to prepare a calibration curve by taking readings with a number of coloured solutions of known concentration covering the required range. This calibration curve remains valid so long as appreciable changes do not take place in the spectral sensitivity of the photoelectric cells, or the colour of the filter. The changes in the cell and in the glass of the filters are generally very gradual and the calibration curve need be checked only at wide intervals, say, every 6 months.

The *advantages* of the " Spekker " absorptiometer are :

(*a*) It is run directly from the electric mains supply—no batteries are required.

(*b*) The readings are independent of the fluctuations of the mains supply.

(*c*) The photo-cells are of the " rectifier " (or " Sperrschicht ") type, and are extremely robust and durable.

(*d*) The scale of the instrument is approximately linear with the concentration of the solution.

(*e*) The instrument readings are not affected by variations in the sensitivity of the cell or of the galvanometer, since a null method is employed.

(*f*) The galvanometer which indicates the photo-electric current is a robust pointer instrument and is used as a null indicator.

(*g*) Readings can be taken with as little as 7 ml. of liquid with a 1 cm. cell ; cells of 4 cm. and 20 cm. length are also available for use with pale-coloured solutions.

V, 5. Turbidimetry and nephelometry.—A coloured material in true solution may be determined by comparison with the colour of a standard—this is the true colorimetric method. The transmission of light is measured and its reflection is zero. With a colloidal dispersion of a coloured precipitate, however, transmission and also some reflection of coloured light occurs. If it can be assumed that the reflection is negligible, then colorimetric methods of determination may be applied ; here we have the phenomenon of **turbidimetry,** and the instrument is used as a **turbidimeter.** If the reflection is very great, colorimetric methods are subject to serious errors : in such a case the *reflection* of the light is measured. The process of measurement is then called **nephelometry,** and the instrument is termed a **nephelometer.** With *white* precipitates, colorimetric procedures cannot be applied and it is necessary to resort to those dependent upon the determination of the reflected light.

It is outside the scope of this volume to give a detailed account of nephelometric apparatus and methods; for these the reader is referred to special treatises on the subject (see Appendix, Section **A, 3**). It may, however, be mentioned that a Duboscq colorimeter may be readily modified for use as a nephelometer; a special nephelometer attachment is also available. The usual cups or tubes are replaced with clear glass tubes with *opaque* bottoms; a powerful artificial light source is employed and the light shining through the side of the standard and unknown sample tubes is reflected upward through the tube and eyepiece. The amount of light is controlled as in colorimetry by variation of the depth of liquid under the plunger. Beer's law is rarely applicable in nephelometry.

V, 6. Determination of the *p*H of solutions by colorimetric methods.—A. Buffer solution method. A series of buffer solutions (Section **I, 20**) is selected, differing successively in *p*H by about 0·2, covering the *p*H range of the solutions under examination. An approximate determination of the *p*H of the liquid is made by the use of a multiple range indicator, *e.g.*, by the B.D.H. universal indicator, or by the systematic use of a number of indicators. This will give the *p*H of the solution within 1 to 2 units, and will indicate the range of *p*H of the buffer solutions required for comparison. Equal volumes, say 10 ml., of the buffer solutions differing successively in *p*H by about 0·2 are placed in a series of test tubes of colourless glass and having approximately the same dimensions, and a small equal quantity of a suitable indicator for the particular *p*H range is added to each tube. A series of different colours corresponding to the different *p*H values is thus obtained. An equal volume (say 10 ml.) of the test solution is treated with an equal volume of indicator to that used for the buffer solutions, and the resultant colour is compared with that of the coloured standard buffer solutions. When a complete match is found, the test solution and the corresponding buffer solution have the same *p*H. Sometimes a complete match is not obtained, but the colour of the test solution falls between those of two successive standards, then it is known that the *p*H value lies between those of the two standards. Further buffer solutions may then be prepared differing by 0·1 *p*H, if desired, and the *p*H value redetermined. As a general rule, colorimetric methods cannot be relied upon to give values of *p*H more accurate than to within 0·2 *p*H unit. For matching the colours, the buffer solutions may be arranged in the holes of a test tube stand in order of *p*H : the test solution is then moved from hole to hole until the best colour match is obtained. Special stands and standards for making the comparison are available commercially. The commercial standards, prepared from buffer solutions, are not permanent and must be checked every six months.

For turbid or slightly coloured solutions, the direct comparison method given above can no longer be applied. The interference due to the coloured substance can be eliminated in a simple way by a device due to H. Walpole (1910). In Fig. 5-13, **A, B, C** and **D** are glass cylinders with plane bottoms standing in a box which is painted a dull black on the inside. **A** contains the coloured solution to be tested (here the test solution + indicator), **B** contains an equal volume of water, **C** contains a solution of known strength for comparison (here the standard buffer solution + indicator), whilst **D** contains the same volume of the solution to be tested as was originally added to **A.** The colour of the unknown solution is thus compensated for.

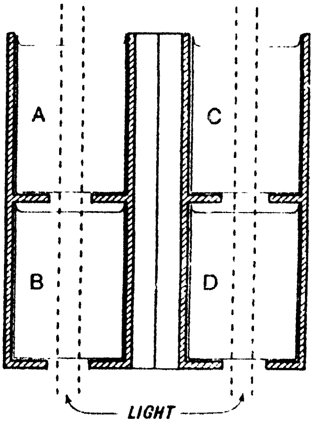

FIG. 5-13.

For details concerning the preparation of buffer solutions, see Appendix, Section **A, 10.**

B. Comparator (or permanent colour standard) method. In this method comparison is made with a series of permanent glass colour standards. Nine glass colour standards are fitted into a disc, and the latter fits into a *comparator*, which is furnished with four compartments to receive small test tubes or rectangular cells, and is also provided with an opal glass screen. The disc can revolve in the comparator, and each colour standard passes in turn in front of an aperture through which the solution in the cell (or cells) can be observed. As the disc revolves, the value of the colour standard visible in the aperture appears in a special indicator recess. The **Lovibond all-purpose comparator*** is shown in Fig. 5-14. A

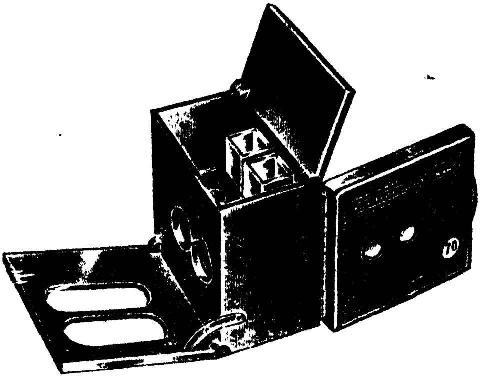

FIG. 5-14.

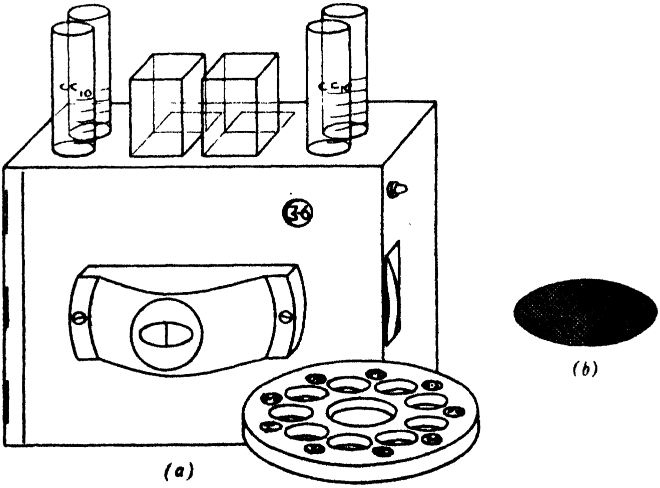

FIG. 5-15.

similar apparatus is manufactured by F. Hellige and Co.† (Fig. 5-15 (*a*)), but this contains a prism attachment by which the two colours being compared are brought side by side in the eyepiece (Fig. 5-15 (*b*)). The range of discs available with the Lovibond all purpose comparator include the following :

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* Reproduced by courtesy of The Tintometer Ltd., Milford, Salisbury, England.

† Supplied by A. Gallenkamp and Co. Ltd., Sun Street, London, E.C.2 England, and by Hellige, Inc., Long Island City, N.Y., U.S.A.

	p*H* *Range*		p*H* *Range*
Cresol red (acid range)	0·2–1·8	Bromo-thymol blue	6·0– 7·6
m-Cresol purple (acid range)	1·0–2·6	Phenol red	6·8– 8·4
Thymol blue (acid range)	1·2–2·8	Cresol red	7·2– 8·8
Bromophenol blue	2·8–4·4	Thymol blue	8·0– 9·6
Bromo-cresol green	3·6–5·2	B.D.H. 9011 indicator	9·0–11·0
B.D.H. 4460 indicator	4·4–6·0	2 : 4-Dinitrophenol (α)	2·8– 4·4
Methyl red	4·4–6·0	2 : 5-Dinitrophenol (γ)	4·0– 5·6
Chloro-phenol red	4·8–6·4	2 : 6-Dinitrophenol (β)	2·8– 4·4
Bromo-cresol purple	5·2–6·8		

It must be pointed out that the Lovibond comparator utilises specially prepared B.D.H. indicators, whilst the Hellige comparator must be employed with Merck's indicators. Neither the discs nor the indicators are interchangeable in the two instruments. An approximate determination of the *p*H of the solution is first made with the B.D.H. universal indicator (which covers the range 4·0 to 11·0) and then a suitable disc is selected. Ten ml. of the unknown solution is placed in the glass test tube or cell, then the appropriate quantity of indicator (usually 0·5 ml.) is added, and the colour produced is matched against the glass disc. Provision is made for the application of the Walpole technique—by the insertion of a " blank " containing the coloured solution. Results accurate to 0·2 *p*H can be obtained.

Mention should be made of the fact that a comparator lamp is available for the Hellige comparator, thus permitting determinations in artificial light. A daylight lamp may also be employed with the Lovibond all-purpose comparator.

Both comparators may also be employed for the colorimetric determination of small amounts of certain elements and radicals, and special colour discs are supplied for this purpose (compare the B.D.H. Lovibond nesslerimeter in Section **V, 4A** ; this instrument is more suitable for very dilute solutions of the constituents under determination).

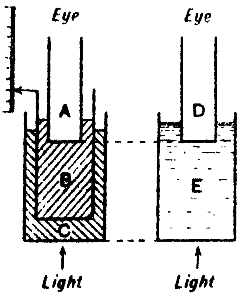

FIG. 5-16.

C. With the hydrogen ion colorimeter. This is a modified form of the Duboscq colorimeter.which utilises a new principle, due to L. J. Gillespie (1921). It is illustrated diagrammatically in Fig. 5-16. The vessels **A, B, C, D** and **E** are of colourless glass with optically plane and parallel bottoms. **A** and **C** are fixed, whilst **B** may be moved up and down. The position of **B** is indicated on a scale, the zero graduation of which corresponds to the position of **B** when **B** and **C** are in contact, and the 100 mark of which corresponds to the position of **B** when **B** is in contact with **A.** If a dilute solution of the acid form of an indicator is placed in **B** and a solution of the same concentration of indicator but transformed completely into the alkaline form be placed in **C,** then it is clear that the position of **B** will determine the ratio of the two forms of the indicator which will be in the field of view. The unknown solution is placed in **E** together with the same concentration of indicator as in **B** and **C.** The auxiliary cups **A** and **D** can be used for compensation by the Walpole technique. **B** is then moved until the two fields are matched ; in this movement the combined depth of the acid and alkaline colours remains the same but their ratio is changed. The *p*H is then calculated with the aid of a simple formula based upon equation (xiii) in Section **I, 27** or can be read from tables. With a good instrument, such as the Bausch and Lomb hydrogen ion colorimeter, which embodies the Gillespie principle, but carried to a point of refinement, readings may be duplicated to within 0·03 *p*H units.*

Reference must also be made to the determination of *p*H, to within 0·01 to 0·04 *p*H units, with the Zeiss Pulfrich photometer and with the Hilger " Spekker " photo-electric absorptiometer. Further details will be found in the pamphlets issued by the manufacturers of these instruments.

V, 7. Some general remarks upon colorimetric determinations.—As a general rule, the maximum error of a visual colorimetric determination is not less than ± 2 per cent and may be as high as ± 8 per cent or more, depending upon the colour response of the observer's eye, the sensitivity of the colour reaction and the method employed in colour matching. With photo-electric equipment and also with the Zeiss Pulfrich photometer it is quite possible to reduce the maximum error of a colorimetric determination to less than ± 0·5 per cent. When determining a minute quantity of a substance, *e.g.*, 0·01 mg., the error of the visual method of colour measurement, even though it may be as high as ± 10 per cent, would be of little practical account and hence photo-electric methods would possess no real advantage except speed of determination. When, however, a colorimetric method is employed for determining a major constituent, such as copper in brass, the increased accuracy obtainable by the use of a photo-electric comparator (or Zeiss Pulfrich photometer) may give the colorimetric determination a status equal to that of a volumetric or gravimetric method of analysis.

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* For further details, see the pamphlet issued by the Bausch and Lomb Optical Co. ; also Snell and Snell, *Colorimetric Methods of Analysis*, 1936, p. 703 (Chapman and Hall).

Reactions, suitable for direct colorimetric determination, which do not suffer interference from other substances—at least to a slight extent—are relatively few. Interference may be avoided by :

(*a*) Suppression of the action of the interfering substance by the formation of complex ions.

(*b*) Removal of the interfering substance by extraction with an organic solvent, *e.g.*, iron may be removed from lead by conversion into ferric chloride and extraction with ether, or by conversion into " ferric thiocyanate " and extraction with amyl alcohol and ether.

(*c*) Isolation of the substance to be determined by the formation of an organic complex which is then removed by extraction with an organic solvent. This method may be combined with (*a*) in which interfering metals are prevented from forming soluble organic complexes by formation of a complex ion and are thus left behind in the aqueous layer.

(*d*) Separation by volatilisation. This is a good method in the few cases where it is applicable, *e.g.*, the distillation of arsenic as the trichloride to separate it from other elements prior to its determination by the Gutzeit method.

(*e*) If the above methods cannot be used, it may be necessary to isolate the substance by the ordinary methods of inorganic analysis ; double precipitation is frequently necessary to avoid errors due to occlusion and coprecipitation.

A general survey of the various methods suitable for colorimetric determinations has been given in Sections **V, 3** to **V, 5.** In the following Sections reference will only be made to the methods requiring the simplest of apparatus (colorimetric titration, standard series, etc.), since such simple apparatus will be available in all laboratories. It should be an easy matter for the student to adapt the selected procedures to the use of other—and more accurate—apparatus. Details for the determination of a number of typical elements and radicals are collected in the following pages ; the list is by no means exhaustive, but will serve to indicate the modern trend of colorimetric methods.

V, 8. Determination of ammonia.—*Discussion.* J. Nessler in 1856 first proposed an alkaline solution of mercuric iodide in potassium iodide as a reagent for the colorimetric determination of ammonia. Various modifications of the reagent have since been made. When Nessler's reagent is added to a dilute ammonium salt solution, the liberated ammonia reacts with the reagent fairly rapidly but not instantaneously to form an orange-brown product, which remains in colloidal solution, but flocculates on long standing. The colorimetric comparison must be made before flocculation occurs. The product has the formula $NH_2Hg_2I_3$ (M. L. Nichols and C. O. Willets, 1934).

The reagent is employed for the determination of ammonia in very dilute ammonia solutions and in water. In the presence of interfering substances, it is best to separate the ammonia first by distillation under suitable conditions (compare Section **III, 20**). The method is also applicable to the determination of nitrates and nitrites : these are reduced in alkaline solution by Devarda's alloy to ammonia, which is removed by distillation. The procedure is applicable to concentrations of ammonia as low as 0·1 mg. per litre.

Nessler's reagent is **prepared** as follows. Dissolve 50 g. of potassium iodide in about 35 ml. of cold ammonia-free water. Add a saturated solution of mercuric chloride until a slight precipitate appears. Add 400 ml. of clear 9*N* sodium or potassium hydroxide. Dilute to 1 litre, allow to stand, and decant from the sediment. Keep stoppered and in a dark place.

Ammonia-free water may be **prepared** in a conductivity water still (compare Section **II, 10C**) or as follows. Redistil 500 ml. of distilled water in a Pyrex apparatus from a solution containing 1 g. of potassium permanganate and 1 g. of anhydrous sodium carbonate ; reject the first 100 ml. portion of the distillate and then collect about 300 ml.

Procedure. For practice in this determination, the student may employ either a very dilute ammonium chloride solution or ordinary distilled water which usually contains sufficient ammonia for the exercise.

Prepare a **standard ammonium chloride solution** as follows. Dissolve 3·141 g. of A.R. ammonium chloride, dried at 100°C, in ammonia-free water and dilute to 1 litre with the same water. This stock solution is too concentrated for most purposes. A standard solution is made by diluting 10 ml. of this solution to 1 litre with ammonia-free water : 1 ml. contains 0·01 mg. of NH_3.

If necessary, dilute the sample to give an ammonia concentration of 1 mg. per litre (Hehner cylinders, Fig. 5-5, are useful for this dilution), and fill a 50 ml. Nessler tube to the mark. Prepare a series of Nessler tubes containing the following volumes of standard ammonium chloride solution diluted to 50 ml.: 1·0, 2·0, 3·0, 4·0, 5·0 and 6·0 ml. The standards contain 0·01 mg. of NH_3 for each ml. of the standard solution. Add 1 ml. of Nessler's reagent to each tube, allow to stand for 10 minutes, and compare the unknown with the standards in a Nessler stand (Fig. 5-2) or in a nesslerimeter (Fig. 5-3). This will give an approximate figure which will enable another series of standards to be prepared and more accurate results obtained (compare Section **V, 4A**).

V, 9. Determination of nitrites.—*Discussion.* When acetic acid solutions of sulphanilic acid and α-naphthylamine are acted upon by nitrous acid, a red colouration is produced which may be used for the colorimetric determination of small amounts of nitrites.* The sulphanilic acid is converted into the corresponding diazo compound which couples with the α-naphthylamine to form α-naphthylamine-*p*-azobenzene-*p*-sulphonic acid, a red azo dye. The full colour does not appear for several hours, but a satisfactory colour comparison can be made after 5 to 10 minutes, provided the sample and standard are treated in the same way.

The **reagent** is *prepared* as follows:

Solution 1. Add 1 g. of A.R. sulphanilic acid to 14·7 g. of glacial acetic acid and 15 ml. of water. Warm until solution is complete, dilute with 300 ml. of water, and stir during the addition.

Solution 2. Add 0·2 g. of A.R. α-naphthylamine to 14·7 g. of glacial acetic acid and 25 ml. of water. Warm until solution is complete, dilute with 300 ml. of water, and stir during the dilution.

Mix equal volumes of the solutions immediately before use.

Standard nitrite solution. Dissolve 4·93 g. of A.R. sodium nitrite in water and dilute to 1 litre. Dilute 10 ml. of this stock solution to 1 litre: 1 ml. of this standard solution corresponds to 0·01 mg. of nitrite nitrogen.

* The colour produced by α-dimethyl-amino-naphthalene is superior in intensity, stability and brilliance to that obtained with α-naphthylamine; it is similarly used to the latter, except that a solution is obtained by dissolution in a solution of 4*N* acetic acid in 95 per cent methyl alcohol. Giblin (1936) has proposed dimethylaniline.

Procedure. For practice in this determination either a very dilute solution of sodium nitrite or ordinary distilled water may be used. If necessary, dilute the sample to give a nitrite concentration of 1 mg. per litre. Prepare a series of Nessler tubes containing the following volumes of the standard nitrite solution diluted to 50 ml. : 0·1, 0·2, 0·4, 0·6, 0·8 and 1·0 ml. Place 50 ml. of the unknown solution in a Nessler tube. To each tube add 2 ml. of the reagent, and stir with a special glass rod (see Section **V, 4B**). After 10 minutes, compare the colours of the tubes. If a closer approximation is required, prepare a fresh series of standards on either side of the first value and repeat the comparison, starting all the tests at the same time.

V, 10. Determination of iron.—*Discussion.* Two methods will be described: the thiocyanate method and the thioglycollic acid method.

A. Thiocyanate method. Ferric iron reacts with thiocyanate to give an intensely-red coloured compound which remains in true solution, whereas ferrous iron does not react. The colour is usually assumed to be due to ferric thiocyanate :

$$Fe^{+++} + 3CNS^- \rightleftharpoons Fe(CNS)_3,$$

but the recent work of H. I. Schlesinger and H. B. V. Valkenburgh (1931) has shown that the red solution contains the complex $[Fe(CNS)_6]^{---}$ ion which is *red.*

$$Fe^{+++} + 6CNS^- \rightleftharpoons [Fe(CNS)_6]^{---}$$

A large excess of thiocyanate should be used since this increases the colour intensity. Strong acids (hydrochloric or nitric acid—concentration 0·05 to 0·5*N*) should be present to suppress the hydrolysis :

$$Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+.$$

Sulphuric acid is not recommended because sulphate ions have a certain tendency to form complexes with ferric ions. Silver, copper, nickel, cobalt, and large quantities of mercury ($>$ 1 g. per litre), zinc, cadmium and bismuth ($>$ 0·1 g. per litre) interfere. Mercurous and stannous salts, if present, should be converted into the mercuric and stannic salts, otherwise the colour is destroyed. Phosphates, arsenates, fluorides, oxalates and tartrates interfere since they form fairly stable complexes with ferric ions ; the influence of phosphates and arsenates is reduced by the presence of a comparatively high concentration of acid.

When large quantities of interfering substances are present, it is usually best to proceed in either of the following ways : (i) remove the iron by precipitation with a slight excess of ammonia solution, and dissolve the precipitate in dilute hydrochloric acid ; (ii) extract the " ferric thiocyanate " three times either with pure ether or, better, with a mixture of amyl alcohol and pure ether (5 : 2) and employ the organic layer for the colour comparison.*

B. Thioglycollic acid method. Thioglycollic acid when added to a solution of a ferrous salt and the mixture rendered alkaline with ammonia solution, produces an intense red colouration. Ferric salts in concentrations greater than 1 in 100,000 yield a transient blue colouration ; this is immediately reduced to a colourless ferrous thioglycollate (I), which then yields the intensely coloured ferrous thioglycollate ion (III) in ammoniacal solution (the thioglycollic acid is oxidised to dithioglycollic acid (II), which gives no colour with either ferrous or ferric iron) :

$$2Fe^{+++} + 2HS.CH_2.COOH \rightarrow 2Fe^{++} + (S.CH_2.COOH)_2 \text{ (II)} + 2H^+.$$

$$Fe^{++} + 2HS.CH_2.COOH \rightarrow Fe(S.CH_2.COOH)_2 \text{ (I)} \rightarrow Fe(S.CH_2.COO)_2^{--} \text{ (III)}.$$

Strong alkalis slowly discharge the colour. A method is thus available for determining both ferrous and ferric iron colorimetrically. The ferric iron is determined with thiocyanate ; the colour is stable in acid solution and is discharged by alkalis. The *total iron* is determined with thioglycollic acid, and the ferrous iron by difference.†

Fluorides, phosphates, arsenates, sulphates, etc., are without effect. Chromium, nickel, cobalt, manganese and uranium interfere, whilst other common metals if present in the order of the concentration of the iron have no effect. Aluminium is rendered innocuous by the addition of excess of citric acid or tartaric acid. Silicates (which have a bleaching effect on the colour) and oxidising agents must be absent.

The thioglycollic acid method is suitable up to a concentration of 1 part in 5,000,000 and the thiocyanate method to several parts per million.

Procedure (**thiocyanate method**). Prepare the following solutions :

1. Standard solution of ferric iron. (*a*) Dissolve 0·7022 g. of A.R. ferrous ammonium sulphate in 100 ml. of water, add 5 ml. of 1 : 5 sulphuric acid, and run in cautiously a dilute solution of potassium permanganate (2 g. per litre) until a slight pink colouration remains after stirring well. Dilute to 1 litre and mix thoroughly. 1 Ml. ≡ 0·1 mg. of Fe. (*b*) Dissolve 0·864 g. of A.R. ferric ammonium sulphate in water, add 10 ml. of concentrated hydrochloric acid and dilute to 1 litre. 1 Ml. ≡ 0·1 mg. of Fe.

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* For experimental details of this process, see Lundell, Hofmann and Bright, *Chemical Analysis of Iron and Steel*, 1931, p. 44 ; see also Section **I, 71B.**

† Ferrous iron may also be determined directly with dimethylglyoxime ; a red colour is produced.

2. **Potassium thiocyanate solution.** Dissolve 40 g. of A.R. potassium thiocyanate in 100 ml. of water ; the solution is *ca.* 4*N*.

Dissolve a weighed portion of the substance in which the amount of iron is to be determined in a suitable acid, and evaporate nearly to dryness to expel excess of acid. Dilute slightly with water, oxidise the iron to the ferric state with dilute potassium permanganate solution or with a little bromine water, and make up the liquid to 500 ml. or other suitable volume. Alternatively, use the iron solution provided by the teacher and oxidise with bromine water. Place 50 ml. of the solution in a Nessler cylinder, and add 5 ml. of the thiocyanate solution and 2 to 4 ml. of 4*N* nitric or hydrochloric acid. Add the same amounts of the reagents to 50 ml. of water contained in another similar Nessler tube, and run in the standard iron solution from a burette (use a long glass tube with bulbed or flattened end for mixing) until the colours are matched ; note the exact volume (x ml.) of the standard iron solution added. Repeat the determination using (50-x) ml. of water. Comparison of the standard and unknown should be made soon after preparation since the colour fades on standing.

Procedure (**thioglycollic method**). The unknown solution is first diluted so as to have a concentration of iron of about 1 part in 500,000. This is best done by testing the unknown solution qualitatively : after a little experience, the intensity of the colour produced will indicate the proportion for dilution.

Place 5 ml. of the solution in a test tube graduated at 5 ml. intervals, add 1 or 2 drops of thioglycollic acid and 0·5 ml. of concentrated ammonia solution. Compare the colour produced with the colours of a series of standards of known concentration of iron which have been similarly prepared. The Lovibond all-purpose comparator is very suitable for this determination (compare Section **V, 5B**).

V, 11. Manganese.—*Discussion.* Small quantities of manganese are invariably determined colorimetrically by oxidation to permanganic acid. The oxidising agents which have been employed include lead dioxide and strong nitric acid, sodium bismuthate, potassium or ammonium persulphate in the presence of a little silver nitrate as catalyst, and potassium periodate. The first two are not very suitable since the excess of the reagent must be removed by filtration. The persulphate method, although widely used, is generally unsatisfactory for, in a number of cases, the reaction proceeds incompletely to the permanganate stage. The periodate method is free from these disadvantages. In hot acid solution, periodate oxidises manganese quantitatively to permanganic acid :

$$2Mn^{++} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+.$$

When ready for test the solution should not contain more than 2 mg. of manganese per 100 ml., otherwise the colour will be too dark and colour matching will be difficult. Frequently ferric iron is added to the standard in amount equal to that found independently to be present in the sample. Phosphoric acid must be present to prevent the precipitation of ferric periodate and iodate and also to decolourise the ferric iron (by complex formation). If chlorides are present, it is necessary to evaporate with a mixture of nitric and sulphuric acids until fumes of the latter appear. Chlorides react with the periodate.

Procedure. For practice in this determination, the manganese content of a suitable steel (1) may be evaluated. Weigh out accurately a suitable quantity of the steel (0·1 to 0·2 g. for steels containing up to 1 per cent of Mn) into a conical flask, dissolve it in 20 to 50 ml. of 1 : 3 nitric acid, and boil for 1 or 2 minutes to expel oxides of nitrogen. Remove from the burner, and add 0·5 to 1·0 g. of A.R. ammonium persulphate ; boil for 10 to 15 minutes to oxidise carbon compounds and to destroy the excess of persulphate. If any permanganate colour develops or oxides of manganese separate, add a few drops of sulphurous acid or sodium sulphite solution to reduce the manganese and render the solution clear, and boil for a few minutes to expel the excess of sulphur dioxide. Dilute the solution to *ca.* 100 ml., add 5 to 10 ml. of A.R. syrupy phosphoric acid and 0·5 g. of potassium periodate (2) : boil for 1 minute and keep hot for 5 to 10 minutes. Cool the solution and make up to 250 ml. in a volumetric flask and mix thoroughly. For a comparison solution, use either a steel of known manganese content which has been similarly treated (3) or a standard solution containing 4·55 ml. of 0·1*N* potassium permanganate diluted to 250 ml. (1 ml. ≡ 0·02 mg. Mn). Any of the methods described in Section **V, 4** may be used for the colorimetric determination ; that utilising a Duboscq colorimeter is particularly suitable.

Notes. 1 Ridsdale's " Mild Steel, No. 1 " (one of the Analysed Samples for Students) or the Bureau of Analysed Samples " Carbon Steel, ' E ' or ' R ' " or British Standardised Steel Sample, No. 11 (supplied by the N.P.L.) may be employed. Suitable steels are also available from the U.S. Bureau of Standard ; see Appendix, Section **A, 8.**

2. Each 0·1 g. of Mn requires 1 g. of potassium periodate.

3. Such standards, containing excess of periodate, are stable for 2 to 3 months.

V, 12. Titanium.—*Discussion.* Hydrogen peroxide produces with an acid solution of titanium sulphate a yellow colour, which is said to be due to pertitanic acid. With small amounts of titanium the intensity of the colour is proportional to the amount of the element present, and therefore forms the basis of a colorimetric method for the determination of titanium. The method is applicable to solutions containing up to 0·1 mg. of TiO_2 per ml. Comparison is usually made with standard titanic sulphate solutions ; two methods for their preparation (from potassium titanium oxalate and potassium fluotitanate) are described below. The hydrogen peroxide solution should be of about 3 per cent strength (10-volume), and the solution should contain at least 5 per cent by volume of sulphuric acid in order to prevent hydrolysis to a basic sulphate and to prevent condensation to metatitanic acid. The colour intensity increases with rise of temperature, hence the solutions to be compared should have the same temperature, preferably 20° to 25°C.

Elements which interfere are : (*a*) iron, nickel, chromium, etc., because of the colour of their solutions ; (*b*) vanadium, molybdenum, cerium, and, under some conditions, chromium, because they form coloured compounds with hydrogen peroxide ; (*c*) fluorine (even in minute amount) and large quantities of phosphates, sulphates and alkali salts (the influence of the last two is largely reduced the greater the concentration of sulphuric acid present—up to 10 per cent). The influence of elements of class (*a*) is overcome, if present in small amount, by matching the colour by the addition of like quantities of the coloured elements to the standard before hydrogen peroxide is added. When large amounts of iron are present, as in the analysis of cast irons and steels, two methods may be adopted : (i) phosphoric acid can be added in like amount to both unknown and standard, after the addition of hydrogen peroxide ; (ii) the iron content of the unknown solution is determined, and a quantity of standard ferric alum solution, containing the same amount of iron, is added to the standard solution. Large quantities of nickel, chromium, etc., must be removed. Elements of class (*b*) must also be removed ; vanadium and molybdenum are most easily separated by precipitation of the titanium with sodium hydroxide solution in the presence of a little iron ; cerium may be eliminated as oxalate. Fluorine has the most powerful effect in bleaching the colour : it must be removed by repeated evaporation with concentrated sulphuric acid. The bleaching effect of phosphoric acid is overcome by adding a like amount to the standard, or by adding 1 ml. of 0·1 per cent uranyl acetate solution for each 0·1 mg. of Ti present.

Procedure. The experimental details for the determination of titanium in a silicate rock (*e.g.*, felspar) and in a cast iron or steel will be given.

Preparation of standard titanium solution. *From potassium titanium oxalate.* Recrystallise the commercial product once from water, if necessary, and dry at room temperature for several days. Transfer 4·5 g. of pure $K_2TiO(C_2O_4)_2,2H_2O$ to a Kjeldahl flask (Section **III, 20**), add 8 g. of ammonium sulphate and 50 ml. of concentrated sulphuric acid, and heat the mixture gradually. Finally boil for 10 minutes to destroy the oxalic acid. Cool, pour the solution into 750 ml. of water, and dilute to 1 litre. Determine the exact titanium content by withdrawing 50 ml. of the solution, then dilute to 200 ml., heat to boiling, and render faintly ammoniacal. Continue the boiling for 2 to 3 minutes. Filter off the precipitated TiO_2,xH_2O on a filter paper, wash with hot water until free from alkali salts, ignite moist in the filter, and weigh as TiO_2. Carry out the determination in duplicate. Calculate the TiO_2 content per ml. of solution.

From potassium titanium fluoride. If necessary, recrystallise the potassium fluo-titanate from water, preferably in a platinum dish, and dry at 105°C ; the salt then has the formula K_2TiF_6,H_2O. Weigh out 1·62 g. of the pure monohydrate into a platinum dish, add 50 ml. of 1 : 1 sulphuric acid, and evaporate nearly to dryness. Cool, wash down the sides of the dish, add more sulphuric acid and again evaporate until most of the sulphuric acid has been removed. Repeat the operation again in order to insure that all hydrogen fluoride is expelled. Cool, transfer quantitatively to a 500 ml. volumetric flask, add sufficient sulphuric acid so that its final concentration in the solution is at least 5 per cent by volume, make up to the mark and mix well. If the initial salt were perfectly pure, the solution would contain 1·00 mg. of TiO_2 per ml. It is best, however, to determine the exact titanium content as above.

A. Titanium in felspar. Dissolve a known weight of the " mixed oxides " (Section **IV, 95, C3**—analysis of a felspar) in sulphuric acid, transfer to a 100 ml. flask, add sufficient sulphuric acid so that the total sulphuric acid content is ultimately 10 per cent, and dilute to within 10 ml. of the mark. If the solution is coloured because of the presence of iron, add sufficient phosphoric acid to decolourise it, and make up to the mark. Prepare a standard solution by placing 80 ml. of 10 per cent sulphuric acid in a 100 ml. standard flask, add the same amount of iron (as ferric alum solution) as is present in the unknown, decolourise by the addition of phosphoric acid dropwise, and make up to the mark. Transfer 50 ml. of each solution to Nessler cylinders, add 3 ml. of 10-volume (3 per cent) hydrogen peroxide to each and mix by means of a long glass tube with a bulb or flattened end. Now add the standard titanium solution from a burette to the blank until after mixing the colours match; note the volume of standard titanium solution employed and add this volume of 10 per cent sulphuric acid to the unknown solution. This will give an approximate value of the titanium content of the solution. More exact values can then be obtained by comparison in a Duboscq or other colorimeter.

B. Titanium in cast iron. Weigh out accurately about 0·5 g. of the cast iron into a 100 ml. conical flask, add 6 ml. of 1 : 3 sulphuric acid, and heat gently until solution is complete; if a cake of solid separates, dissolve it in a few ml. of water. When solution is complete,* cool somewhat, and add 10 ml. of 1 : 1 nitric acid. Heat until fumes of sulphur trioxide are evolved, and cool to room temperature. Transfer the solution to an accurately graduated 25 ml. test tube or flask, rinse the flask 2 or 3 times with a little dilute sulphuric acid (1 : 20), and add water to the 25 ml. mark. Filter through a dry filter paper into a 30 ml. test tube: do not wash the tube or the paper.

Take an aliquot portion (10, 15 or 20 ml.) of the clear filtrate, and add syrupy phosphoric acid dropwise until the solution is decolourised. Add 3 ml. of 10-volume (3 per cent) peroxide, mix, and compare in a colorimeter against a standard sample of iron* which has been treated exactly as the unknown sample. The simplest procedure is to add to the tube of lighter colour a standard solution of titanium from a micro-burette and to the other add similar amounts of 1 : 20 sulphuric acid until the colours match when the solutions are well mixed. The percentage of titanium may then be calculated from the titanium content of the iron and the titre of the standard titanium solution.

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* An insoluble residue of silica can be " fumed " off with hydrofluoric acid, followed by treatment with concentrated sulphuric acid to remove excess of the former acid. Large quantities of iron (*e.g.*, in ferro-silicon, etc.) are best handled as ferric chloride by extraction with an organic solvent prior to the titanium determination.

V, 13. Vanadium.—*Discussion.* When hydrogen peroxide is added to a solution containing small quantities of vanadium (up to 0·1 mg. of V per ml.) and 15 to 20 per cent of its volume of sulphuric acid, a reddish-brown colouration is produced ; this is usually attributed to the formation of "pervanadic acid." This forms the basis of the colorimetric procedure for the determination of vanadium. The method is not so satisfactory as for titanium. The colouration is intensified by strong acids and a large excess of hydrogen peroxide tends to bleach the colour, hence the experimental conditions must be rigorously controlled. The vanadium must be in the quinquevalent state.

The colour is unaffected by moderate amounts of hydrofluoric acid ; this acid is therefore sometimes employed to prevent interference by small quantities of titanium. The method is not applicable in the presence of elements which give colourations with hydrogen peroxide, such as titanium, molybdenum and cerium ; tungsten also interferes and must be removed. Iron can be decolourised by the addition of either phosphoric or hydrofluoric acids. In the presence of elements which yield coloured solutions, such as chromium or nickel, it is best to add equal amounts of these elements to the standard solution. If steel is being analysed, the most convenient procedure is to use a like steel as standard.

Procedure (**vanadium in steel**). Prepare a *standard solution of vanadium* by dissolving 1·146 g. of A.R. ammonium vanadate NH_4VO_3 in water and making up to 1 litre ; 1 ml. contains 0·5 mg. of V.

Dissolve 1 g., accurately weighed, of the steel in 50 ml. of 1 : 4 sulphuric acid. When solution is complete, introduce 10 ml. of concentrated nitric acid, and boil until nitrous fumes are no longer evolved. Dilute the solution to 100 ml. with hot water, heat to boiling and add saturated potassium permanganate solution until a pink colour persists or a precipitate is formed.* Boil for 5 minutes. Filter off on asbestos any tungstic oxide or manganese oxide which may be precipitated. Add a slight excess of freshly prepared sulphurous acid, and boil off the excess. Cool, add 5 ml. of syrupy phosphoric acid and 5 ml. of 10-volume hydrogen peroxide.

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* Such standards may be obtained from the Bureau of Analysed Samples, Middlesbrough, England, or from the U.S. Bureau of Standards, Washington.

Simultaneously with the first decomposition prepare in an analogous manner a comparison solution from a standard steel which contains no vanadium, but is otherwise similar. Alternatively, prepare a comparison solution from a plain carbon steel and add appropriate amounts of solutions of chromium, nickel, etc., if the unknown contains these elements.

Transfer the two solutions to 100 ml. Nessler cylinders, and treat the blank with standard ammonium vanadate solution, added from a burette, until the colours match. Allow 2 minutes for the development of the colour. A more precise comparison may be made with a Duboscq colorimeter or with the other apparatus of Section **V, 4.**

V, 14. Chromium.—*Discussion.* Small amounts of chromium (up to 0·05 per cent) may be determined colorimetrically by comparing the colour of chromates in alkaline solution; uranium interferes. A **standard solution of chromium** is prepared by dissolving 0·2555 g. of A.R. potassium chromate and 0·1 g. of A.R. sodium carbonate in water and diluting to 1 litre; 1 ml. corresponds to 0·1 mg. Cr_2O_3.

A better method is to employ **diphenylcarbazide** $CO(NH.NH.C_6H_5)_2$ (Cazeneuve's reagent, 1900). In acid solution chromates form a soluble violet compound with this reagent; the test is sensitive to 1 part in a million or better. Cadmium, magnesium, mercury, molybdenum, copper, lead, silver, gold, zinc, nickel and cobalt interfere; permanganates, if present, may be removed by boiling with a little alcohol.

Procedure. Prepare the **diphenylcarbazide reagent** by dissolving 1 g. of diphenylcarbazide in 100 ml. of alcohol containing a trace of sulphuric acid. The standard chromium solution is made as detailed in the *Discussion.*

Faintly acidify a definite volume (x ml.) of the liquid containing the chromate (0·02 to 0·5 mg. of Cr) with sulphuric acid, add 2 ml. of the reagent and 20 ml. of 1 : 1 sulphuric acid. Match the colour against that obtained by adding the standard chromate solution from a micro-burette to a mixture of x ml. of water, 2 ml. of the reagent, and 20 ml. of 1 : 1 sulphuric acid (for further details, see Section **V, 4B**).

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* Alternatively, add 20 ml. of 1 per cent silver nitrate solution, heat to boiling, and add slowly, while stirring, a concentrated solution of ammonium persulphate until a permanent pink colour develops. If no pink colour is obtained, add a few drops of 2 per cent potassium permanganate solution. Boil for 5 minutes.

V, 15. Aluminium.—*Discussion.* Aluminium salts give a bright red lake when treated with the ammonium salt of aurin tricarboxylic acid ("**aluminon**") in the presence of an acetic acid-acetate buffer. If the concentration of the aluminium is small (up to 0·05 mg. in 50 ml.), a coloured liquid (faint pink to deep red according to the concentration of the aluminium) is obtained, which is suitable for the colorimetric determination of aluminium.

The chief interfering element is iron—even minute amounts give a purplish-red tint—and must be entirely removed: this is most simply effected by extraction as thiocyanate with ether-amyl alcohol or with amyl alcohol alone (compare Section **V, 9A**). Bismuth, lead, antimony, stannic tin, mercuric mercury, titanium and silicic acid give white precipitates. Large amounts of alkaline or rare earths, of basic acetates or hydroxides of chromium, cerium, thorium and zirconium give red lakes, and phosphates also interfere; these are either dissolved or decolourised by the addition of ammonium carbonate solution. Reducing agents must be absent.

Procedure. Prepare the **aluminon reagent** by dissolving 0·2 g. of ammonium aurin tricarboxylate in 100 ml. of water. Prepare also the **standard aluminium solution** by dissolving 1·759 g. of A.R. potassium aluminium sulphate $K_2SO_4,Al_2(SO_4)_3,24H_2O$ in water and diluting to 1 litre; 1 ml. contains 0·1 mg. Al.

Prepare 20 to 50 ml. of a clear, dilute hydrochloric acid (2 parts of concentrated acid : 98 parts of water) solution that is free from iron, from appreciable concentrations of salts that interfere because of their colour, and, preferably, from substances, other than aluminium, that are precipitated by ammonium carbonate solution. The solution should contain not more than 0·05 to 0·1 mg. of Al. Add 10 ml. of 1 : 3 acetic acid, 5 ml. of the reagent, and finally a 10 per cent solution of ammonium carbonate in 1 : 2 ammonia solution slowly and with constant stirring until an excess of 5 to 10 ml. is present. Compare the colour produced with standards containing known amounts of aluminium until a match is obtained.

The following procedure, due to Scherrer and Mogerman (1938), is superior to the above and is particularly well adapted to the determination of small quantities of aluminium in non-ferrous alloys, such as solders, bearing metals, etc.

Interfering elements are completely removed by the use of the mercury cathode cell shown in Fig. 4-13 (*c*) ; here the anode consists of a platinum wire, 1 mm. in diameter, which projects about 12 cm. into the solution, and the anolyte and mercury are simultaneously vigorously stirred by the use of a stirrer carrying two blades so situated that one is immersed in the anolyte and the other in the mercury. With about 50 ml. of mercury and a current of 3 amps., 1 g. of copper or iron can be removed in about 45 minutes and 1 g. of tin, antimony, lead, zinc, etc. in 2 to 3 hours.

Dissolve a convenient weight of the alloy in an appropriate acid. Sulphuric acid is the best acid to employ, if possible ; if solution is effected with nitric acid, the latter must be removed by gentle fuming with sulphuric acid : the final content of sulphuric acid should not exceed 20 per cent by volume. Dilute the solution to 25 ml., filter off any lead sulphate which has separated, and wash the filtrate into a mercury cathode cell and electrolyse. When electrolysis is complete, separate the electrolyte from the mercury whilst the current is kept on. The volume of the solution should now be from 40 to 75 ml. Add 5 ml. of concentrated hydrochloric acid, 5 ml. of glacial acetic acid and 5 ml. of the aluminon reagent. Mix well whilst cautiously adding concentrated ammonia solution until the solution becomes clear, although still acid to litmus and still deeply coloured. Place a piece of litmus paper against the inner surface of the beaker, and, while stirring constantly, add concentrated ammonia solution at a rate of about 1 drop every 2 seconds until about 2 ml. has been added ; then add 1 drop every 3 or 4 seconds until the litmus paper turns blue. Add 5 ml. of glacial acetic acid, allow to stand for 5 minutes, and neutralise as just described. Finally add 5 ml. of concentrated ammonia solution. When the solution has cooled to room temperature, compare the colour obtained with that of solutions of known aluminium content which have been similarly prepared.

V, 16. Molybdenum.—*Discussion.* The method for the colorimetric determination of up to 1 per cent of molybdenum, particularly in steels, is based upon the brown colouration produced by the formation of molybdenum thiocyanate in an acid medium. The brown colouration is extracted by ether, butyl acetate or *cyclo*hexanol—the last-named is the best solvent—and the colour compared with standards which have been similarly prepared.

Nickel, chromium, vanadium, silicon and copper do not interfere in the percentages usually encountered in steel, although if the copper content is greater than 0·13 per cent it is necessary to separate the insoluble copper thiocyanate before estimating the molybdenum.

Procedure (**molybdenum in steel**). Prepare the following reagents :

Sodium or potassium thiocyanate solution. Dissolve 10 g. of A.R. sodium or potassium in 200 ml. of water.

Stannous chloride solution. Heat 50 g. of stannous chloride crystals with 40 ml. of concentrated hydrochloric acid until dissolved, and dilute with 240 ml. of water. Preserve over metallic tin to prevent re-oxidation.

***cyclo*Hexanol.** Redistil the purest commercial *cyclo*hexanol, and collect the fraction b.p. 158° to 160°C. Shake 50 ml. of *cyclo*hexanol with 5 ml. of the thiocyanate and 25 ml. of the stannous chloride solutions in a separating funnel, and discard the aqueous solution. This reagent must be prepared freshly as required.

Standard molybdenum solution. Heat 0·71 g. of A.R. molybdic acid (containing 85 per cent MoO_3) with 100 ml. of concentrated nitric acid and 30 ml. of concentrated hydrochloric acid until dissolved. Add 100 ml. of water, boil, cool, and dilute to 2000 ml. The molybdenum content (about 0·2 mg. per ml.) may be computed from the weight of molybdic acid employed, but is best determined in 50 ml. of solution as lead molybdate (Section **IV, 23A**).

Dissolve 0·1 g. of the sample of steel (or iron) and also a standard sample* of the same weight in 5 ml. of nitric acid, sp. gr. 1·13, and 5 ml. of 60 per cent perchloric acid (**DANGER,** see Section **IV, 70**) in 150 ml. beakers provided with raised clock glasses or with Fisher "speedyvap" beaker covers.† Boil for 10 minutes until copious white fumes commence to be evolved, cool, and dissolve in 15 ml. of water. Add 5 ml. of the thiocyanate solution to each beaker, and transfer to 100 ml. separating funnels, rinsing the beakers first with 10 ml. of the stannous chloride solution and then with 10 or 15 ml. of the *cyclo* hexanol. Shake the funnels for 1 minute and reject the aqueous solution. Add 5 ml. of the thiocyanate solution and 15 ml. of stannous chloride solution, and shake again for 1 minute. Draw off the wash solutions, and filter if an appreciable quantity of insoluble cuprous thiocyanate is present. Transfer to similar colour comparison tubes, and add the *cyclo*hexanol saturated with thiocyanate and stannous chloride solutions from a burette until the colours of the tubes are identical. The weight of molybdenum in the sample and standard is then directly proportional to the volumes (compare Section **V, 3C**).

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* For example, either the U.S. Bureau of Standards Cr-Mo steel, No. 72a or a similar molybdenum-free steel to which a known amount of the standard molybdenum solution has been added.

† For stainless steels it may be necessary to use also 5 ml. of 1 : 1 hydrochloric acid.

V, 17. Nickel.—*Discussion.* This element may be determined with dimethylglyoxime (compare Section **IV, 12**), but since the nickel complex is sparingly soluble, only minute amounts of nickel may be determined colorimetrically by this process, for otherwise the complex precipitates. Ferrous iron, which gives a red colour with the reagent, interferes and must be removed ; the interference of small amounts of cobalt is prevented by the addition of excess of ammonia solution. The sensitivity of the reaction is about 1 part in 500,000 parts of solution, but may be increased by the addition of hypochlorite or hypobromite prior to the addition of the reagent. The coloured complex formed after oxidation is, however, quite soluble in water. Interference from small amounts of iron and aluminium may be prevented by the introduction of Rochelle salt into the solution ; cobalt and phosphates also interfere and must be removed. This modified method is suitable for the determination of 0·1 to 1·0 mg. of nickel in 100 ml. of solution.

Procedure. Prepare the **dimethylglyoxime reagent** by dissolving 1 g. of dimethylglyoxime in 100 ml. of rectified spirit. Prepare the **standard nickel solution** by dissolving 0·673 g. of pure nickel ammonium sulphate in water and diluting to 1 litre : 1 ml. contains 0·1 mg. of Ni. The solution may be further diluted to a basis of 0·01 mg. of Ni per ml., if necessary.

Prepare the nickel solution, containing not more than 1·0 mg. of nickel and free from interfering elements. Render it slightly ammoniacal, dilute to 100 ml. with water, add 1 ml. of 1 per cent sodium hypochlorite solution or of saturated bromine water, followed by 5 ml. of the reagent and mix. Compare the resulting colour with standards similarly prepared. The colour develops to its maximum intensity in a few minutes.

V, 18. Cobalt.—*Discussion.* α-Nitroso-β-naphthol (compare Section **IV, 33A**) may be employed for the determination of cobalt for concentrations between 0·01 and 0·1 per cent; a red colouration is produced with the reagent and 1 part of cobalt in 1,000,000 parts of solution may be detected.

Iron, aluminium and chromium are kept in solution by the addition of ammonium citrate. Copper, nickel and manganese, and also preferably iron, should be removed; nickel can be precipitated with dimethylglyoxime or, better, with the specific reagent α-benzildioxime and the excess of the latter destroyed. Nitrates must be absent. β-Nitroso-α-naphthol has been recommended and is said to be 8 times more sensitive than α-nitroso-β-naphthol.

Procedure. Prepare the **α-nitroso-β-naphthol reagent** by boiling 0·1 g. of α-nitroso-β-naphthol with 20 ml. of water and 1 ml. of a *N* sodium hydroxide solution, filter and dilute to 200 ml. Prepare the **standard cobalt solution** by dissolving 0·477 g. of A.R. cobalt sulphate $CoSO_4,7H_2O$ in water and diluting to 1 litre; 1 ml. contains 0·1 mg. of Co. The solution may be diluted 10-fold to a basis of 0·01 mg. of Co per ml. if required.

Treat the faintly acid (hydrochloric acid) solution (*ca.* 80 ml.) containing not more than 0·1 mg. of cobalt, with 5 ml. of a solution containing ammonium citrate and ammonium hydroxide (50 g. of citric acid dissolved in 25 ml. of water and 50 ml. of concentrated ammonia solution) and dilute to 100 ml. Add 5 ml. of the freshly-prepared reagent and mix thoroughly. Compare the colour produced with those of standards that have been subjected to the same treatment; it is best to use the balancing method (Section **V, 4D**).

V, 19. Arsenic.—*Discussion.* Very small amounts of arsenic (0·001 to 0·1 mg.) are best determined by volatilising the element as arsine AsH_3, and comparing its reaction under certain experimental conditions with that obtained by the use of known amounts of arsenic. Various reactions have been proposed: that due to Marsh utilises the formation of the mirror of arsenic produced by the action of heat, whilst that due to Gutzeit compares the colourations formed upon discs of dry paper impregnated with mercuric chloride. A modification of the original Gutzeit method will be described.

The reduction to arsine is best effected electrolytically in an apparatus incorporating a mercury cathode or, more simply, by the older process with arsenic-free zinc and hydrochloric acid. Both procedures are given below.

An alternative method, due essentially to C. R. Sanger and O. F. Black (1907), replaces the disc by a thin *strip* of mercuric bromide paper : the arsenic content is given both by the depth of the tint and also by the length of the paper bearing the stain.

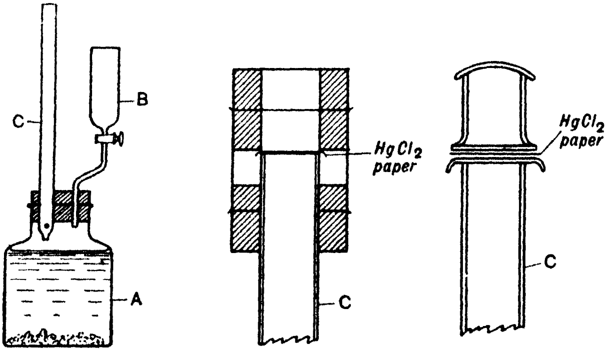
The arsenic must be in the tervalent state. Nitric acid, the halogens, and compounds that yield sulphur dioxide, hydrogen sulphide or phosphine must be absent. The last-named are readily eliminated by boiling with nitric acid ; the excess of the latter is removed by evaporation with sulphuric acid to fumes of sulphur trioxide. In such treatment the arsenic becomes quinquevalent and must be reduced, *e.g.*, with ferrous sulphate solution. The following metals and their salts are undesirable : silver, mercury, platinum, palladium, nickel, cobalt and copper. In the presence of interfering substances, it is usually best to separate the arsenic first as the trichloride by distillation in an all-glass apparatus from a solution containing hydrochloric acid and a reducing agent, such as hydrazine sulphate.

Procedure. Prepare a **standard arsenic solution** by dissolving 1·00 g. of A.R. arsenious oxide in the minimum volume of pure sodium hydroxide solution, acidify with dilute hydrochloric or sulphuric acid, and make up to 1 litre : 1 ml. contains 1 mg. of As_2O_3. A solution containing 0·001 mg. As_2O_3 per ml. is prepared by diluting 1 ml. of this solution to 1 litre.

Prepare the **sensitised mercuric chloride papers** by immersing Whatman arsenic test strips or strips cut from Whatman No. 20 paper in a 5 per cent solution of A.R. mercuric chloride in 95 per cent alcohol, and dry them on a horizontal rack of glass rods at the laboratory temperature out of exposure to direct sunlight. Keep them in a desiccator over calcium chloride in the dark until required.

Prepare the **lead acetate papers** by soaking filter papers (10 cm. by 5 cm.) in a 10 per cent solution of lead acetate in recently boiled water ; dry the papers and keep them in a closed tube. (These will serve to retain any hydrogen sulphide which may be evolved in the apparatus.)

A. Zinc and acid method. Fit up the apparatus shown in Fig. 5-17 (*a*). **A** is a wide-mouthed bottle of about 100 ml. capacity fitted with a 2-holed rubber bung. A small tap funnel **B** is inserted into one of the holes, and a glass tube **C,** 20 cm. in length and 5 to 7 mm. internal diameter and drawn out at the lower end to an aperture of about 2 mm., is passed through the other hole : a hole of about 2 mm. diameter is made in **C** (below the cork) to allow of the free escape of the gases. The upper end of **C** is ground smooth (*e.g.*, on a fine carborundum stone) at right angles to the tube, and is fitted with a device whereby the mercuric chloride paper is held firmly in position over the opening of the tube, thus ensuring that all the arsine evolved passes through the paper and a uniform circular stain is produced. The simplest of these is to fit a wide tube (about $\frac{3}{4}''$ long and *ca.* 1″internal diameter) round the upper part of **C** by means of a cork and also to provide another cork, bored with a hole equal in diameter to the external bore of the tube, which fits tightly on to the flat end of **C.** A circle of mercuric chloride paper (about 10 mm. in diameter) is cut out by means of a cork borer and placed on top of the tube; the paper is held firmly in position by inserting the other bored cork (see Fig. 5-17 (*b*)). A. J. Lindsey (1930) has developed an all glass apparatus* (Fig. 5-17 (*c*)) which serves the same purpose; the tube is 20 cm. long, with internal bore 5 mm. or 6·5 mm., and is provided with a flange and two ears at the upper end. The paper is placed on this flange and is held securely in position by means of a cap with an identical flange, the upper part of which is worked into a double-lipped shape; the cap and tube are held together by means of a pair of rubber bands.



(*a*) (*b*) (*c*)

FIG. 5-17.

Roll one of the prepared lead acetate papers in the form of a cylinder 10 cm. in length and place it so that the upper end is not less than 2·5 cm. below the upper end of the tube ; alternatively, the tube may be packed with strips of the lead acetate paper about 10 cms. in length.

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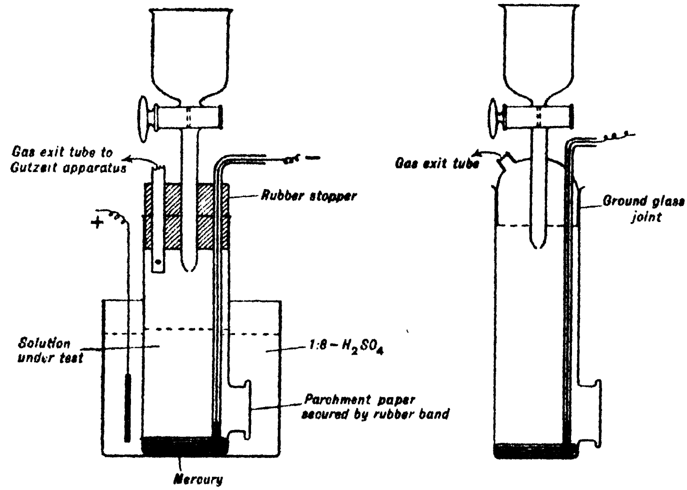
* Supplied by Baird and Tatlock (London) Ltd., 16-17 Cross Street, London, E.C.1, England.

Prepare a **series of standard stains,** covering a range of, say, 0·001 to 0·05 mg. of As, as follows. Place 5 to 10 g. of arsenic-free zinc (*e.g.*, A.R.) in the bottle together with about 0·5 g. of A.R. stannous chloride. Fit the apparatus together, and place one of the prepared discs of mercuric chloride paper into position as described above. Introduce 2 ml. of the arsenic solution (0·001 mg. per ml.) into the flask, and then run in 50 to 55 ml. of 2·5*N* sulphuric or hydrochloric acid (prepared from the A.R. acids), and close the tap. Immerse the bottle in a large beaker of water containing water at room temperature. Allow the reaction to proceed for 1 hour, then remove the mercuric chloride paper disc and dry it in the dark on a sheet of filter paper. Repeat the procedure with fresh discs, using increasing amounts of arsenic solution. Mark each disc clearly with the exact arsenic content.

If the standards are likely to be used frequently, a fair degree of permanence may be secured by any of the following procedures : (i) dry the discs between filter paper, dip them into cellulose varnish, mount on a sheet of white paper, and preserve over calcium chloride in a desiccator in the dark ; (ii) dip the discs into molten paraffin wax, and preserve them over phosphoric oxide in a closed tube which is kept in the dark ; (iii) immerse the discs in a 10 per cent solution of potassium iodide until the red colour of mercuric iodide at first produced disappears, leaving a brown stain, and then dry in the dark on a sheet of filter paper. Prepared papers are available commercially, which are claimed to preserve their permanence for 1 year.

If the arsenic content of the solution is approximately known, the solution is added to zinc and stannous chloride contained in the bottle, dilute sulphuric or hydrochloric acid introduced, and the determination carried out exactly as in the preparation of the standards. If the arsenic content is entirely unknown and interfering substances are absent, a preliminary test should be carried out as follows. Set up the apparatus, add the acid to the zinc, and then run in the arsenic solution in suitable quantities at a time, commencing with 1 ml. and waiting 15 minutes after each addition until a stain is produced within the range of standards. The procedure is then repeated in the manner used in preparing the standards, taking the appropriate amount of the arsenic solution. The reagents should first be tested for the presence of arsenic by running a blank with distilled water.

B. Electrolytic (mercury cathode) method. A mercury cathode cell, due to T. Callan and Jones (1930), suitable for the determination of small quantities of arsenic, is shown in Fig. 5-18 (*a*).



(*a*) (*b*)

Fig. 5-18.

It consists of a flat-bottomed tube, 5″ long and 1-3/8″ in diameter, having an aperture of 1″ diameter blown on the side about ¼″ from the bottom of the tube. The aperture is covered by a piece of parchmentised paper,* which acts as an efficient diaphragm of very low electrical resistance between the catholyte and anolyte. The aperture is flanged so that the parchment paper may be held in position by means of a rubber band. Purified mercury is placed in the bottom of the tube so that its surface is just below the level of the aperture. Electrical connexion is made with the mercury by means of a narrow glass tube, into the lower closed end of which is sealed a short platinum wire. The whole of the exposed platinum wire dips into the mercury ; a little mercury is placed inside the the tube and a copper wire dipping into this forms the negative terminal of the cell. The narrow tube, carrying the cathode lead, passes through a 3-holed rubber stopper which closes the cell. The rubber stopper also carries a tap funnel of 20 ml. capacity, through which the electrolyte or test solution may be introduced, and also an exit tube having a small hole near the bottom and which is connected directly with the purifying tube of the Gutzeit apparatus (not shown). The cathode cell is immersed in the electrolyte of the anode cell (1 : 8 sulphuric acid), which is itself immersed in a cooling bath maintained at room temperature. The anode is a sheet of platinum foil (2″ by 1″) welded to a short length of thick platinum wire.

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* Parchmentised paper is prepared by rapidly immersing Whatman No. 1 filter paper in pure 80 per cent sulphuric acid for a few seconds, and then washing with water. The paper is stored under water until required.

Fig. 5-18 (*b*) shows the essential parts of the same apparatus, but with the rubber stopper replaced by a ground-glass joint.*

In use a current of 2 amps. is passed for 15 minutes, followed by 4 amps. for 15 minutes. In other respects the procedure for the determination is similar to that given in **A.**

C. Modified Sanger-Black-Gutzeit method. Prepare the **sensitised mercuric bromide paper** as follows. Dry some Whatman arsenic tests strips No. 130 (120 × 2·5 mm. or 150 × 5 mm.) or strips prepared from Whatman No. 20 paper in an electric oven at 105°C for 1 hour, and store in a desiccator over calcium chloride until required. Saturate the strips with a 0·35 per cent† solution of pure mercuric bromide in 95 per cent ethyl alcohol, allow them to drain, and dry in a desiccator for 10 minutes. The strips are then ready for use : no treated strips should be stored for longer than 2 hours before use.

Prepare a **ferric ammonium sulphate solution** by dissolving 8·4 g. of A.R. iron alum with 1 ml. of 1 : 4 A.R. sulphuric acid in 100 ml. of water. Ten ml. of this solution contains the equivalent of *ca.* 0·5 g. Fe_2O_3.

Prepare a **stannous chloride solution** by dissolving 16 g. of A.R. stannous chloride in 20 ml. of water containing 1 ml. of A.R. hydrochloric acid (sp. gr. 1·2).

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* Both forms of apparatus are obtainable from Baird and Tatlock (London) Ltd., Cross Street, London, E.C.1, England.

† Formerly more concentrated solutions (up to 5 per cent) of mercuric bromide were employed. The weaker the solution, the longer and the less intense will be the stain.

H. E. Crossley (1936) obtained satisfactory results by the use of " Swedish " filter paper No. 1F : strips, without previous drying, were immersed in a 1·5 per cent solution of mercuric bromide in 95 per cent ethyl alcohol, then drained for 5 minutes on a rack of glass rods, and finally kept in a desiccator over calcium chloride for 2 hours before use. He utilised strips of 115 × 2·5 mm. size for As contents of 0·002 to 0·018 mg. and obtained lengths of stains from 9 to 72 mm. ; for As contents of 0·005 to 0·045 mg., he employed strips of 115 × 5·0 mm and the corresponding lengths of stains were 13 to 95 mm. A 60 ml. generating bottle was used in both cases, but with the higher arsenic contents the upper tube is of slightly larger bore to accommodate the wider strip ; reaction was allowed to take place for 45 minutes, The apparatus used is shown in Fig. 5-19. It consists of a 60 ml. wide-mouthed bottle into the mouth of which is fitted by means of a rubber stopper a tube 12 cm. long and 1·25 cm. in diameter and constricted 5 cm. from the top. The lower part of the tube contains a roll or strips of heavy filter paper soaked in 10 per cent lead acetate solution and dried (this filter paper is held in position by a plug of purified glass wool, which also serves to remove acid spray); the upper portion contains purified glass wool soaked in the same solution. This tube is connected by a rubber stopper to a glass tube 10 cm. long and 4 mm. internal diameter which is constricted 4 cm. from the lower end; the strip of test paper is placed in this tube. In order to obtain uniform results which are independent of the temperature of the laboratory, a small water condenser, through which water below 20°C is circulated, surrounds the tube containing the test-strip.

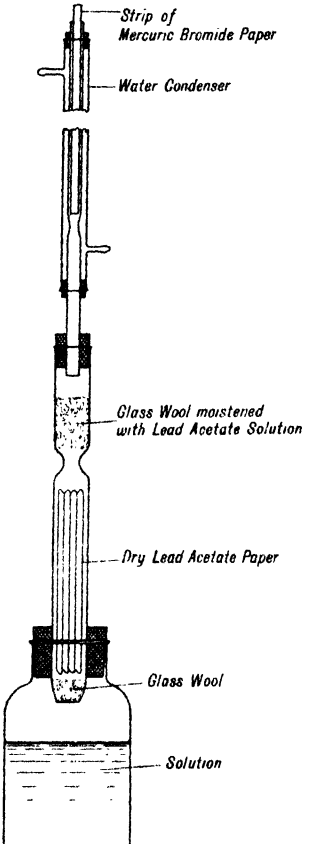
Strip of Mercuric Bromide Paper
Water Condenser
Glass Wool moistened with Lead Acetate Solution
Dry Lead Acetate Paper
Glass Wool
Solution
Zinc

FIG. 5-19.

Place the solution under test (containing not more than 0·02 mg. of As_2O_3) in the generating bottle, add sufficient acid so that the acid content is equivalent to 4·2 to 6·3 g. of sulphuric acid, then introduce 2 ml. of the ferric solution* and 0·5 ml. of the stannous chloride solution: dilute to 50 ml. Introduce about 15 g. of arsenic-free zinc (preferably in the form of shot, 1/3 to 1/6″ mesh). Immediately insert the connecting tubes, and place the mercuric bromide strip (120 × 2·5 mm.) in position; shake the bottle gently and allow to stand for 60 minutes. The temperature should be maintained at 20° ± 1°C (or, less satisfactorily, at 25° ± 1°C) by immersing the bottle in a water bath or a large beaker containing water at this temperature. Remove the strip, dry it between sheets of filter paper, dip it into either cellulose varnish or into molten paraffin wax (free from water), and mount it on a sheet of white paper. Compare the stain produced with stains obtained in the same manner by known amounts of arsenic, using portions of a standard solution containing 0·001, 0·002, 0·004, 0·006, 0·01, 0·015, and 0·02 mg. of As_2O_3 and adding water, acid, etc., so as to have the same volume and concentration as the final unknown solution. The strips bearing the standard stains should be mounted on a sheet of white paper, folded back to form a cylinder and preserved in a closed test tube containing phosphoric oxide in the dark. A blank determination must of course be carried out with the reagents ; this should show not more than 0·001 mg. of As_2O_3. Instead of direct comparison with standards, the lengths of the stains by a given procedure may be plotted on a graph and values interpolated ; results accurate to 5 per cent are obtained.

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* Ferrous iron prevents polarisation between the zinc and acid, and hence accelerates the liberation of the arsine.

For the determination of quantities of arsenic varying between 0·02 mg. and 0·5 mg. of As_2O_3, a larger apparatus is employed. The bottle has a capacity of 250 ml., the lower tube is 15 cm. long and of 1·5 cm. diameter with a constriction 6 cm. from the upper end, whilst the upper tube is 18 cm. long and of 7·5 mm. bore and is constricted 9 cm. from the lower end. The strips of paper should be 150 × 5 mm. and are similarly prepared with a 3·5 per cent solution in 95 per cent ethyl alcohol. The final volume of the solution in the bottle should be 200 ml. and should contain an equivalent of 18·5 g. of sulphuric acid and 0·1 g. of ferric oxide and also 0·5 ml. of the stannous chloride solution ; about 40 g. of A.R. zinc is required and reaction is allowed to continue for 40 minutes. The standard stains should be prepared with 0·02, 0·05, 0·1, 0·2, 0·3, 0·4 and 0·5 mg. of As_2O_3. The quantity of the unknown solution employed should be such as to contain between 0·02 and 0·5 mg. of As_2O_3.

V, 20. Antimony.—*Discussion.* The most satisfactory method for the colorimetric determination of small amounts (up to 0·5 mg.) of antimony is the potassium iodide-pyridine method (S. G. Clarke, 1928), and is particularly well adapted to the determination of antimony in tin. The preliminary separation is effected by deposition on copper foil (Reinsch's reaction). The deposit is dissolved in sodium peroxide solution, and any dissolved copper is precipitated by hydrogen sulphide in the alkaline solution and the copper sulphide removed by filtration. The solution is acidified with sulphuric acid and evaporated to fuming ; the residue is diluted with water and to it are added aqueous solutions of pyridine, sulphur dioxide, potassium iodide, and gum arabic or " starch glycerite."* The yellow colouration is then compared against standards similarly prepared.

Tin and arsenic when present in moderate amounts (several centigrams) do not interfere. Bismuth and several other heavy metals give a coloured precipitate, whilst zinc yields a white crystalline precipitate : these metals should therefore be absent. The best acid to employ is sulphuric acid. Hydrochloric acid and particularly chlorides bleach the colour. Excessive amounts of sulphurous acid cause liberation of iodine, whilst a large excess of pyridine produces colour fading.

Procedure. Full details for the determination of small amounts of antimony (0·001 to 0·05 per cent) in tin will be given.

Prepare a **standard solution of antimony** by dissolving 0·2764 g. of A.R. tartar emetic in 1000 ml. of 10 per cent sulphuric acid ; 1 ml. contains 0·1 mg. of Sb.

Weigh out accurately a suitable quantity of tin (1 to 5 g. according to the antimony content, which should be *ca.* 0·5 mg.) into a 750 ml. conical flask ; add 50 ml. of concentrated hydrochloric acid and sufficient bromine to ensure an excess while the tin is dissolving. When the tin has dissolved, add 2 to 10 g. of oxalic acid (according to the amount of antimony), followed by about 350 ml. of water. Boil the liquid gently : the oxalic acid will dissolve and yield a solution tinged with bromine. Add about 0·5 g. of sodium hypophosphite to reduce all the free bromine, to separate completely any arsenic which may be present, and to render the solution colourless. Introduce a flat open spiral of copper (made from a strip of clean copper foil, 15 × 2 cm.) into the solution ; it should stand upright on the bottom of the flask. Boil for 2 hours, remove the copper coil by means of a hooked glass rod, and wash it successively with a gentle stream of 5 per cent hydrochloric acid and of water. Place the coil in a small beaker, cover it with water, add 1 to 2 g. of pure sodium peroxide, and warm until the deposit is dissolved and the copper is well darkened by oxidation. Pour off the solution from the coil, and then rinse it with water. Pass hydrogen sulphide into the solution and washings for 15 seconds, allow the small precipitate of copper sulphide to coagulate on the water bath (15 minutes) and filter ; wash with a dilute solution of ammonium nitrate. Add 5 ml. of concentrated sulphuric acid and a few drops of concentrated nitric acid to the filtrate and washings, evaporate just to fuming, cool and add 15 ml. of water. The antimony in the resultant solution (*ca.* 20 ml.) is determined colorimetrically as follows.

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* This is prepared by heating starch with glycerine and diluting with water. This (and also gum arabic) is added as a protective colloid to stabilise the suspension of the yellow complex. It also gives a bluish-green colouration with free iodine, and then will indicate whether the solution is completely reduced by the sulphur dioxide added.

Introduce the reagents in the order given into a 100 ml. Nessler cylinder : 10 ml. of 1 per cent gum arabic solution, 5 ml. of 20 per cent potassium iodide solution, 1 ml. of 10 per cent aqueous pyridine, 1 ml. of sulphur dioxide solution prepared by 10-fold dilution of a saturated aqueous solution, and 60 ml. of cold 1 : 3 sulphuric acid. The antimony solution prepared as above is then added, the beaker being rinsed with not more than 5 ml. of water, and the whole stirred with the special glass stirrer (see Section **V, 4B**). Run the standard antimony solution from a burette into another Nessler tube containing similar quantities of the reagents (except that 80 ml. of 1 : 3 sulphuric acid are used instead of 60 ml.) until the colours match after the solution has been well stirred. The final adjustment is made by adding a small quantity of water to make the volumes in the two Nessler tubes equal. Not more than 10 ml. of the standard antimony solution should be required for otherwise the colour will be too deep for accurate comparison. A blank determination should be made on the reagents.

V, 21. Tin.—*Discussion.* A dilute solution of stannous tin (concentration $\not>$ 30 mg. per litre) gives a blue colouration with an acid molybdate solution. The composition of the " molybdenum blue complex " appears to be fixed if the concentration of the tin does not exceed 30 mg. litre ; this forms the basis of a method for the colorimetric determination of tin. The solution should be cold, nearly neutral and free from excessive amounts of neutral salts ; a trace of phosphoric or arsenic acid makes the complex more stable. Antimony, and oxidising and reducing agents must be absent.

Procedure. Prepare a **standard solution of tin** by dissolving 1·00 g. of A.R. tin in 100 ml. of 1 : 1 hydrochloric acid and dilute to 1 litre with the same acid ; 1 ml. contains 1 mg. of Sn. For the preparation of more dilute solutions, dilution should be effected with 1 : 1 hydrochloric acid. Prepare the **molybdate reagent** by dissolving 1 g. of A.R. molybdenum trioxide in a little sodium hydroxide solution, acidify the solution with hydrochloric acid, and dilute to 200 ml.

Treat the acidified solution containing up to 1 mg. of tin with a little pure aluminium, and boil in an atmosphere of carbon dioxide to reduce the element completely to the stannous condition. Take a measured volume of the solution, add 2 ml. of the molybdate reagent and, after 1 minute, 10 ml. of amyl alcohol ; this will extract the whole of the blue coloured compound. Separate the amyl alcohol layer, clarify—if necessary—by the addition of 1 ml. of ethyl alcohol, and compare with standards similarly prepared.

V, 22. Lead.—*Discussion.* For the determination of minute quantities of lead (0·005 to 0·25 mg.) advantage is taken of the fact that when a sulphide is added to a solution containing lead a brown colour, due to the formation of colloidal lead sulphide, is produced.

Interference is produced by the presence of (*a*) neutral salts, such as ammonium chloride and particularly tartrates and citrates, and (*b*) other metals, such as copper, bismuth, iron and aluminium. Errors due to (*a*) may be allowed for by ensuring that the standards for comparison contain amounts of salts approximately equal to those in the solution under test, whilst those produced by (*b*) are eliminated by the usual analytical procedure or by the use of diphenylthiocarbazone (see below). The disturbing effect due to copper and iron if present in small amount may be overcome by the addition of a few drops of a 10 per cent aqueous solution of potassium cyanide ; aluminium may be retained in ammoniacal solution by the addition of ammonium citrate solution, a corresponding amount of the latter being added to the standards.

In case of doubt as to the presence of other metals it is best to isolate the lead quantitatively by means of **diphenylthiocarbazone** $C_6H_5.NH.NH.CS.N = NC_6H_5$ (**"dithizone"**). The reagent consists of a solution in carbon tetrachloride or, preferably, chloroform in which it is more soluble, and yields a red colouration with minute quantities of lead salts. A number of metals interfere, but the reaction of most of these, with the exception of bismuth, is inhibited by the addition of aqueous potassium cyanide solution. The lead complex is removed by extraction with chloroform, but the resultant coloured lead compound is not well adapted for colorimetric determination ; the organic lead complex is oxidised and the lead is ultimately determined by the colloidal sulphide method.

Procedure. Prepare a **standard lead solution** by dissolving either 0·183 g. of A.R. lead acetate crystals or 0·160 g. of A.R. lead nitrate in 100 ml. of water ; 10 ml. of this are diluted to 100 ml. for a working solution, of which 1 ml. contains 0·1 mg. of Pb.

As an illustration of the simple lead sulphide procedure, the **determination of lead in commercial tartaric acid** will be described. Dissolve 10 g. of the tartaric acid in about 40 ml. of hot water, add 5 to 6 drops of 10 per cent potassium cyanide solution, then 25 ml. of 1 : 2 ammonia solution (which should make the solution ammoniacal), and finally 2 to 3 drops of ammonium sulphide solution (prepared by saturating 1 : 4 ammonia solution with well-washed hydrogen sulphide). Make up to 100 ml. Match the solution thus prepared against a standard solution made by treating 10 g. of lead-free tartaric acid in exactly the same way and adding to it 2 ml. of the standard lead solution. If the acid being tested yields an appreciably darker colour than the standard, a smaller quantity of it should be taken and subjected to a similar treatment. A darker standard should not be used.

The following is a general procedure and is based upon the use of **dithizone.** If organic matter is present, destroy it by digestion with sulphuric and nitric acids, dilute, and evaporate to fuming to remove the nitric acid. Cool the residue, dilute and treat successively with 2 g. of citric acid, ammonia solution until alkaline, and 1 ml. of 10 per cent potassium cyanide solution. The solution should now have a volume of 100 to 150 ml. Extract it in a small separating funnel with three successive portions (10 ml., 5 ml., 5 ml.) of a freshly prepared solution of 0·1 g. of diphenylthiocarbazone in 100 ml. of chloroform ; continue to extract with small portions of solution (say, 2 ml.) until the extract no longer has a red colour. Wash each extract in succession with 10 ml. of water, combine the extracts, and distil off the solvent. Destroy the organic part of the residue by heating with 0·5 ml. of concentrated sulphuric acid and a few drops of nitric acid. Dissolve the residue in water, add 2 g. of A.R. ammonium acetate, ammonia solution until alkaline, 1 ml. of 10 per cent potassium cyanide solution, and 0·1 ml. of 10 per cent sodium sulphide solution. Compare the colour developed with standards similarly prepared (and also containing 2 g. of ammonium acetate) from the standard lead solution.

V, 23. Copper.—*Discussion.* Potassium ferrocyanide reacts with very dilute neutral solutions of copper salts to yield a purplish-brown colouration due to copper ferrocyanide. In the presence of ammonium nitrate, the reaction will serve to detect 1 part of copper in 2,500,000 parts of water, and may be used as a basis for the colorimetric determination of small quantities of copper (up to 0·5 mg.).

The solution should be neutral, for free acid lessens the colour and changes it from a purplish-brown to an earthy-brown. If acid, it is rendered slightly alkaline with ammonia solution and the excess of ammonia boiled off ; if alkaline, because of the presence of caustic alkalis, the solution is barely acidified by an acid and then treated with a little ammonia solution, etc. Lead, when present in too large a quantity, has little effect upon the colour. Iron interferes, however, but can be removed as follows. The solution is treated with a few drops of concentrated nitric acid to oxidise the iron to the ferric state, and the iron is subjected to a double precipitation with ammonia solution in the presence of 1 g. of ammonium sulphate. The filtrate and washings are boiled to remove ammonia completely and the copper determined in the residual solution.

A more sensitive reagent is **sodium diethyldithiocarbamate** $(C_2H_5)_2N.CS.SNa$ (T. Callan and J. A. R. Henderson, 1929), which yields a golden-brown colouration with minute amounts of copper salts. It will detect 1 part of copper in 50,000,000 parts of solution. The colour is produced in either neutral, acid or ammoniacal solution.

The reaction is not specific for copper : a number of other metals, when present in appreciable quantity, give a white turbidity or colouration. Thus silver, lead, mercury, cadmium, antimony, tin, aluminium, chromium and zinc yield white turbidities, whilst bismuth, iron, manganese, nickel and cobalt give rise to coloured compounds. Lead may be removed as sulphate. Separation from iron may be effected either by double precipitation with ammonia solution as in the ferrocyanide method given above or by precipitation of the copper as sulphide at pH 3. The best procedure, however, appears to be to extract the coloured copper complex with carbon tetrachloride : iron is retained in solution by ammonia and ammonium citrate solutions, but bismuth must be removed first.

Procedure. Prepare a **standard copper solution** by dissolving 0·3928 g. of A.R. crystallised copper sulphate in 1 litre of water ; 1 ml. contains 0·1 mg. of copper. For the dithiocarbamate method, it is best to dilute this solution 10-fold.

A. Ferrocyanide method. The duplication method (Section **V, 4B**) is often employed for this determination. Secure two 100 ml. Nessler cylinders and place 5 drops of a 4 per cent aqueous A.R. potassium ferrocyanide solution in each. Add a measured quantity of the *neutral* solution (free from interfering elements) in which copper is to be determined to one of them ; fill both to the mark with distilled water. Add 5 ml. of 10 per cent A.R. ammonium nitrate solution to each, and then the standard copper solution from a burette to the blank until the colours in both cylinders match ; stir the liquid well after each addition. The exact volume of the standard copper solution added is noted and from this the amount of copper in the unknown solution can be calculated. For further general details, see Section **V, 4B.**

B. Sodium diethyldithiocarbamate method. The copper solution should be free from interfering elements and should contain not more than 0·05 to 0·08 mg. of copper ; it should also be either ammoniacal or acid with nitric acid. Place a known volume of the copper solution in a Nessler cylinder, add 10 ml. of a 0·1 per cent aqueous solution of the reagent and make up to 100 ml. Compare the colour produced by the standard series method (Section **V, 4A**) with that of standards prepared in exactly the same way. The addition of a little protective colloid, *e.g.*, gelatin, to the solutions increases their brilliance, and facilitates accurate comparison of the colours.

If the extraction method is to be employed, proceed in the following manner. If iron is present, convert it into the ferric state, add 2 g. of citric acid and render alkaline with ammonia solution. Then add 10 ml. of a 0·1 per cent aqueous solution of the reagent, and extract four times with three 5 ml. portions of pure carbon tetrachloride—the final extract should be colourless. Compare the colour produced with that of solutions containing known quantities of copper treated in a similar manner.

V, 24. Bismuth.—*Discussion.* When potassium iodide solution is added to a dilute sulphuric or nitric acid solution containing a small amount of bismuth, a yellow colouration, due to the formation of a complex iodide, is produced. This is suitable for the colorimetric determination of quantities up to about 1 mg. of bismuth.

The solution must be free from large amounts of lead, copper, tin, arsenic, antimony, gold and silver, and from elements in sufficient quantity to colour the solution, *e.g.*, nickel. Substances which liberate iodine from potassium iodide interfere, for example, ferric iron ; the latter should be reduced by sulphur dioxide and the excess of gas boiled off. Separation of bismuth from copper is best effected by making use of the insolubility of bismuth phosphate in dilute nitric acid.

For the determination of bismuth in lead, the latter is precipitated as sulphate in the presence of tartaric acid (to prevent coprecipitation of the bismuth), the tartaric acid is destroyed by wet oxidation with nitric and sulphuric acids, the nitric acid eliminated by evaporation to fuming, the solution diluted, and sulphurous acid and potassium iodide solution added. The yellow colour is then compared with standards similarly prepared.

Procedure. Prepare a **standard solution of bismuth** by dissolving 0·105 g. of A.R. bismuth* in 20 ml. of concentrated sulphuric acid, and dilute to 1 litre with water ; 1 ml. contains 0·1 mg. of Bi.

Treat the colourless solution (20 to 30 ml.), containing not more than 0·5 to 1 mg. of bismuth and free from interfering substances but acid with sulphuric acid, with 1 ml. of a saturated solution of sulphur dioxide, 10 ml. of a 30 per cent solution of potassium iodide, and dilute to 50 ml. Match the yellow colour produced against standards containing the same concentration of sulphuric and sulphurous acids. After the determination add starch solution to make sure that the colours are not partially due to free iodine.

V, 25. Silver.—*Discussion.*—*p*-Dimethylamino-benzalrhodanine $(CH_3)_2N.C_6H_4.CH{=}\underline{C.CO.NH.CS.S}$ gives a pink to red colouration with small quantities of silver, and may be used for its colorimetric determination in solutions containing 0·06 to 9 mg. per litre. Soft soda glass adsorbs silver, and it is best to employ silica apparatus ; Pyrex glass-ware may be used for determinations at room temperature, but cannot be employed for the evaporation of silver-containing solutions. The method is particularly useful for the determination of silver in drinking water, swimming pools, or those cases where silver has been employed as a sterilising agent.

Cuprous copper, mercurous mercury, gold, platinum and palladium interfere. Calcium carbonate, sodium nitrate and ammonium nitrate increase the depth of colour due to silver if any of them are present in concentrations greater than 1 mg. per litre. Very small amounts of either sulphuric acid or of potassium sulphate (0·6 g. per litre for the latter) also increase the depth of the rhodanine colour. Chlorides, even when present in small amounts, cause a fading of the colour ; they are removed by 2 or 3 evaporations of the solution in a silica vessel with concentrated nitric acid.

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* Obtainable from the Mallinckrodt Chemical Works, New York, U.S.A. ; see, however, Appendix, Section **A, 9.**

Procedure. Prepare a series of suitable standards from A.R. silver nitrate. Treat the neutral solution, containing not more than 9 mg. of silver per litre and free from the interfering substances mentioned above, with 0·5 ml. of 4*N* nitric acid and sufficient water to make the volume 15 ml. Mix thoroughly, add 0·5 ml. of a 0·02 per cent alcoholic solution of *p*-dimethylamino-benzal-rhodanine, and mix again to develop the pink or red colour. Match the colour against standards similarly prepared from silver nitrate solution.

V, 26. Silicate.—*Discussion.* Small quantities of dissolved silicic acid react with a solution of a molybdate in a mineral acid medium to give an intense yellow colour, due probably to the complex acid $H_8[Si(Mo_2O_7)_6]$. The colour is similar to that of potassium chromate solutions, which can therefore be used for the preparation of permanent standards for the colorimetric determination of silicates. The method is applicable up to about 50 mg. of silica per litre.

Phosphates and arsenates give similar colourations and should best be absent ; it is said, however, that small amounts of phosphates do not interfere, but it is best to remove them by magnesia mixture or render them inactive by the addition of ammonium citrate. Reducing substances, such as ferrous iron and hydrogen sulphide give a blue colour, and must therefore be removed. Iron in greater concentration than 20 mg. per litre interferes. Water used for dilution must be freshly distilled, for it dissolves significant traces of silica on standing in glass.

The method is chiefly employed for the determination of silica in water supplies and natural waters, and its use in this connexion will be described.

Procedure. Prepare the **standard comparison solution** by dissolving 0·630 g. of A.R. potassium chromate in 100 ml. of water ; 1 ml. of this solution is equivalent to 1 mg. of SiO_2.

Prepare the **reagent** by dissolving 30 g. of A.R. ammonium molybdate in 200 ml. of 1 : 1 hydrochloric acid and 400 ml. of water.

Place 50 ml. of the sample of water into a Nessler tube, and add 5 ml. of the molybdate reagent. Stir thoroughly, and after 10 to 15 minutes compare the yellow colour developed with the chromate standard as follows. To a similar Nessler cylinder containing 50 ml. of water* add the standard chromate solution (*x* ml.) from a burette until the colour matches that of the unknown solution. Repeat the determination by placing (50-*x*) ml. of water (or of 0·5 per cent borax solution) in the Nessler cylinder, and add the chromate solution until the colour matches again. One ml. of the standard chromate solution corresponds to 1 mg. of SiO_2 per 50 ml. of the sample or 20 mg. per litre of sample.

V, 27. Determination of other elements and radicals.—Space does not permit the inclusion of a detailed account of the determination of small quantities of other elements and radicals. The following Table refers to selected methods which are available for elements and radicals not already discussed, and reference is made to standard works where full details will be found.

1 = E. D. Snell and C. R. Snell, *Colorimetric Methods of Analysis*, Vol. I (1936).

2 = N. H. Furman and W. W. Scott, *Standard Methods of Chemical Analysis*, Vols. I and II (1939).

3 = J. H. Yoe, *Photometric Chemical Analysis*, Vols. I and II (1928).

Element or Radical	*Method or Reagent*	*Details in*
Mercury	(*a*) Mercuric sulphide	1, 3
	(*b*) Diphenyl-carbazone	1
Thallium	(*a*) Thallous sulphide	1
	(*b*) Thallous phosphomolybdate	1
Gold	(*a*) Prister's method	1, 2, 3
	(*b*) Cassel's method	1, 2, 3
	(*c*) Moir's method	1, 2, 3
Platinum	(*a*) Complex iodide	1, 3
Beryllium	(*a*) Quinalizarin (1 : 2 : 5 : 8-tetrahydroxy-anthraquinone)	1
Cerium	(*a*) Gallic acid	1
Zinc	(*a*) Zinc sulphide	1
	(*b*) Zinc ferrocyanide	1, 3
Calcium	(*a*) Alizarin	1, 2
	(*b*) Picrolonic acid	1
Magnesium	(*a*) " Magneson " (para-nitrobenzene-azo-resorcinol)	1
	(*b*) Curcumin	1
Sodium	(*a*) Sodium uranyl zinc acetate	1

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* It is better to use 50 ml. of 0·5 per cent A.R. borax solution, as the colour is then more stable and more easily reproducible.

Element or Radical	*Method or Reagent*	*Details in*
Potassium	(*a*) Potassium chloroplatinate and reduction with stannous chloride	1, 3
	(*b*) Potassium sodium cobaltinitrite	1
Chloride	(*a*) Silver chloride	1
Chlorine	(*a*) *o*-Tolidine	1, 2
	(*b*) Benzidine	1
Chloramine	(*a*) *o*-Tolidine	1
	(*b*) Nessler's reagent	1
Bromide	(*a*) Schiff's reagent	1, 2
	(*b*) Free bromine and carbon tetrachloride	1, 3
	(*c*) Fluorescein	1
Iodide	(*a*) Palladous chloride	1
	(*b*) Starch-iodine reaction	1
	(*c*) Bromine water	1
Fluoride	(*a*) Bleaching effect upon oxidised titanium solution	1, 2, 3
	(*b*) Zirconium oxychloride and purpurin (1 : 2 : 4-trihydroxy-anthaquinone)	1, 2
Cyanide	(*a*) Ferric thiocyanate	1, 3
	(*b*) Prussian blue	1, 3
	(*c*) As ammonia by Nessler's reagent	1
Oxygen	(*a*) Ammoniacal cuprous chloride	1, 2, 3
	(*b*) Starch-iodine complex	1
	(*c*) Indigo-carmine	1
Hydrogen peroxide	(*a*) Oxidation of ferrous iron, followed by thiocyanate reaction	1, 3
	(*b*) Ammonium molybdate	1, 3
Ozone	(*a*) Fluorescein	1
	(*b*) Destruction of nitrite	1
Nitrate	(*a*) Sodium diphenylamine sulphonate	1, 2
	(*b*) As ammonia by Nessler's reagent	1, 3
	(*c*) Phenol disulphonic acid	1, 3
Phosphate	(*a*) Phosphomolybdate, reduction with stannous chloride	1
	(*b*) Phosphomolybdate, reduction with hydroquinone	1, 3
Borate	(*a*) Turmeric paper	1, 2, 3
	(*b*) Curcumin	1, 3
Sulphide	(*a*) Lead sulphide	1, 2, 3
	(*b*) *p*-Amino-dimethyl-aniline (methylene blue method)	1, 3
Sulphate	(*a*) Barium sulphate	1
	(*b*) Benzidine	1

CHAPTER VI

GAS ANALYSIS

VI, 1. General discussion.—The *methods of gas analysis* may be classified as follows :—

1. Volumetric methods.* A measured volume of the gas mixture, at a known temperature and pressure, is subjected to selective chemical reactions (absorbents) to remove the various constituents in succession, the quantities so removed being determined by the resultant diminution in volume. When there is no suitable absorbent for the gas to be determined (*e.g.*, methane), it is frequently possible to mix it with excess of another gas (*e.g.*, oxygen) with which it reacts chemically (often in the presence of a catalyst) and under proper conditions to determine the change in volume which takes place.

In a precision form of apparatus, due to Bone and his co-workers (see Section **VI, 6E**), the gas is expanded to a fixed volume and the pressure exerted is measured, as is also the diminution in pressure of the gas after each absorption when expanded to the same fixed volume. The constant volume method may also be employed with the Ambler portable apparatus (Section **VI, 6D**).

2. Titration methods. The constituent sought is absorbed in a liquid reagent of known concentration. This method is frequently employed for gases, such as sulphur dioxide, which are soluble in water. An interesting example is the determination of small quantities of carbon monoxide by passage over heated iodine pentoxide :

$$I_2O_5 + 5CO = 5CO_2 + I_2 ;$$

the liberated iodine is titrated with dilute standard sodium thiosulphate solution.

3. Gravimetric methods. The gas is absorbed by, or reacts with, a weighed amount of the reagent, or else is absorbed in a liquid and a precipitate is subsequently weighed. Thus sulphur is determined in coal gas (Referees' method) by burning a known volume in a special Bunsen burner ; the air for the combustion passes over a shelf containing ammonium sesquicarbonate and the liberated ammonia carries the sulphur dioxide with it. The gases are absorbed in water, the resultant solution treated with a little pure bromine, acidified with dilute hydrochloric acid, warmed to remove excess of bromine, and the sulphur determined by precipitation as barium sulphate in the usual manner.

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* The term volumetric in this connexion is restricted to processes in which *gas* volumes are measured.

4. Physical methods. The constituents are determined by measurement of their physical properties, such as density, thermal conductivity, viscosity and refractivity.

The following account of gas analysis is intended merely as an introduction to the subject, and will be considered under two headings: (*a*) analysis of gaseous mixtures, and (*b*) the determination of the volume of a gas produced in a chemical reaction and its application to the analysis of solids and liquids. For further details, the reader is referred to the standard text books on gas analysis (see Appendix, Section **A, 3**).

VI, 2. Sampling.—The first step in the analysis of a gaseous mixture is the collection of a representative sample of the gas

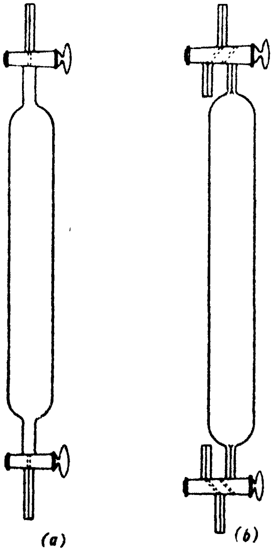

FIG. 6-1.

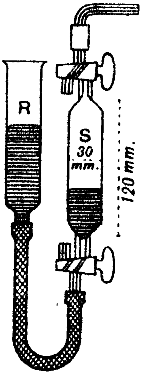

FIG. 6-2.

in a suitable vessel. If a large quantity of the gas is available it may be either passed or aspirated through a sample tube of the type shown in Fig. 6-1 (*a*) or (*b*). The former has two

2-way capillary taps ; the latter has two 3-way capillary stopcocks, which permit the flushing out of the connecting tubes with the sample itself or with a confining liquid. When the quantity of gas available is limited, the apparatus shown in Fig. 6-2 may be used : the connexions are cleared of air by blowing or aspirating some of the gas through the upper tap, or alternatively by evacuating the connexions from the same place and filling them with mercury. The gas is collected in **S** by lowering the reservoir **R.**

If a sample of the gas is to be collected and kept for analysis for a considerable time, the portions of gas taken for analysis must be displaced with mercury. A small gasometer that is suitable for prolonged storage is shown diagrammatically in Fig. 6-3. The gas is contained in the large glass bulb **A,** which carries a capillary U-tube **B** at the top, and at the bottom is connected to the levelling bulb **C** by means of a rubber tube ; the capillary is closed by means of a rubber tube and pinch-cock **D.** The apparatus is first filled with mercury : by lowering or raising the levelling bulb, gas can be drawn in or driven out as desired. If the gas sample is to be kept for some time, the capillary tube **B** is filled with mercury by inserting a small pipette at **D.** A simple gasometer may also be constructed from a round-bottomed flask fitted with a 2-holed rubber stopper and bent glass tubes as shown in Fig. 6-4 : the right-hand tube is connected to a levelling bulb by means of rubber tubing as in Fig. 6-3.

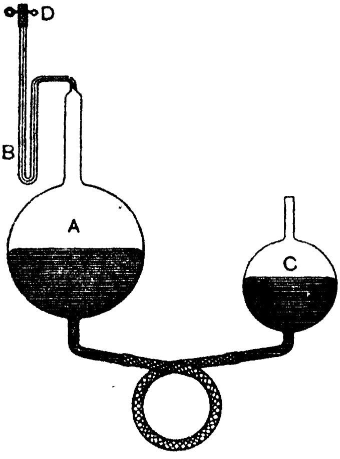

Fig. 6-3.

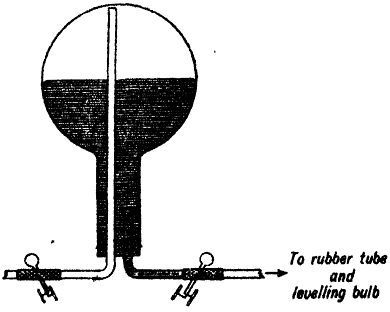

Fig. 6-4.

VI, 3. Purification of mercury.—The mercury employed in analysis should be carefully purified. If impure, it clings to the glass, and accurate readings are impossible. The principal impurities in ordinary mercury are copper, cadmium and zinc. The impurities are largely removed by allowing the mercury to run in a fine stream through a long length of 5 per cent nitric acid in the apparatus shown in Fig. 6-5. A glass tube of about 1 inch bore and 20 to 30 inches length is fused to an S-shaped glass capillary of about 2 mm. bore. The main tube is filled with 5 per cent nitric acid, and the siphon is so shaped that the bottom of the tube always contains a little mercury. An ordinary funnel containing a filter paper folded in the usual way is supported above the apparatus with the stem just dipping into the nitric acid. A small hole is then made in the apex of the filter paper by means of a pin, and the mercury poured into the filter. The mercury usually takes a zig-zag course as it flows in the form of a fine spray through the dilute acid; any dust, etc., contaminating the mercury is retained in the filter, together with a little mercury. The mercury collects in the bottom of the tube, and siphons over into the collecting bottle or beaker. The process should be repeated a second time, and the mercury finally passed through a column of water in a similar apparatus. The mercury may be dried by heating to 100° to 150° C (preferably under reduced pressure) **in a fume cupboard provided with an efficient draught. MERCURY VAPOUR IS HIGHLY POISONOUS AND THE EFFECT IS CUMULATIVE;** hence exposure of mercury to the open atmosphere should be reduced to the absolute minimum and all operations with mercury at elevated temperatures must be conducted in a fume cupboard. All bottles containing mercury should be stoppered.

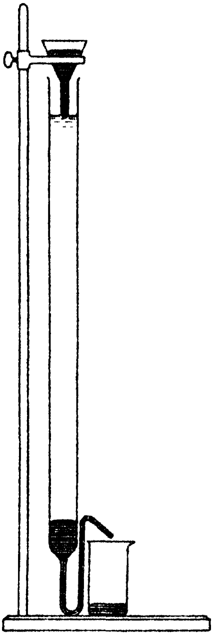

Fig. 6-5.

For most purposes the mercury obtained by the above process is suitable for use. If mercury is to be used for calibrating measuring apparatus, it is best distilled under reduced pressure in a slow stream of air; under these conditions the volatile metals, cadmium, zinc, etc., form nonvolatile oxides, and complete purification of the mercury from these metals can be obtained.

All apparatus utilising mercury should be set up on a wooden base having a raised edge, which will serve to retain any mercury spilt during any of the operations. The base should be provided with a small hole, ordinarily closed with a cork, through which the mercury may be swept and recovered. For picking up spilled globules of mercury, the special pipette shown in Fig. 6-6 is useful : suction may be applied by filter pump or mouth through a rubber tube. The bulb forms a reservoir or safety trap.

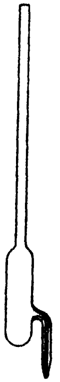

FIG. 6-6.

VI, 4. Correction of volume of gas for temperature and pressure.—The volume of a gas depends upon the temperature and pressure to which it is subjected. In all cases where a gaseous volume is measured the observed volume must be reduced to the corresponding value under normal conditions of temperature and pressure. The most generally employed temperature is 0°C, and the most generally employed pressure is that due to a column of mercury 76·0 cm. in height and of density 13·596 (*i.e.*, at 0°C) : these are usually termed N.T.P. The variation of the density of mercury over the range 0°C to 30°C is 0·0738, thus an error of about 0·5 per cent would be introduced by a variation of 30°C of the temperature of the barometer. Table XXV contains the values of the density of mercury at various temperatures.

TABLE XXV. DENSITY OF MERCURY (IN GRAMS PER ML.)

Temp. °C.	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*14*	*16*	*18*
−20°	13·645	13·640	13·635	13·630	13·625	13·620	13·615	13·610	13·605	13·600
0°	13·596	13·591	13·586	13·581	13·576	13·571	13·566	13·561	13·556	13·551
20°	13·546	13·541	13·536	13·532	13·527	13·522	13·517	13·512	13·507	13·502
40°	13·497	13·492	13·488	13·483	13·478	13·473	13·468	13·463	13·458	13·453
60°	13·449	13·444	13·439	13·434	13·429	13·424	13·420	13·415	13·410	13·405
80°	13·400	13·395	13·390	13·386	13·381	13·376	13·371	13·366	13·362	13·357
100°	13·352									

The formula for applying the correction is :

$$H_0 = H_t\{1 - (\beta - \alpha)t\},$$

where H_t is the height of the barometer at t°C, H_0 is the reduced height at 0°C, β is the coefficient of linear expansion of mercury, and α is the coefficient of expansion of the material of the barometer scale.

If V is the volume of *dry* gas measured at a pressure of P mm. of mercury (corrected for temperature as already explained) and a temperature of t°C, then it follows by application of Boyle's and Charles' laws that the volume V_0 at N.T.P. is given by:

$$V_o = V \times \frac{P}{760} \times \frac{273.}{(273 + t)}$$

If the gas is measured wet, *i.e.*, saturated with water vapour, the pressure P must be *reduced* by the vapour pressure of water at the temperature of the measurement. Table XXVI contains the values of the vapour pressure of water at various temperatures.

TABLE XXVI. PRESSURE OF AQUEOUS VAPOUR (IN MM. OF MERCURY).

Temp. °C	*Pressure.*	*Temp.* °C.	*Pressure*	*Temp.* °C.	*Pressure.*
0°	4·60	10°	9·17	20°	17·39
1°	4·94	11°	9·79	21°	18·50
2°	5·30	12°	10·46	22°	19·66
3°	5·69	13°	11·16	23°	20·89
4°	6·10	14°	11·91	24°	22·18
5°	6·53	15°	12·70	25°	23·55
6°	7·00	16°	13·54	26°	24·99
7°	7·49	17°	14·42	27°	26·51
8°	8·02	18°	15·36	28°	28·10
9°	8·57	19°	16·35	29°	29·78
				30°	31·55

When the determinations are made rapidly and comparative values only are required (as in a technical analysis), the correction for temperature and pressure is often omitted, provided no appreciable variations have occurred during the analysis. It may be mentioned that a variation of 7 mm. in pressure or of 3°C in the temperature introduces an error of the order of 1 per cent in the percentage analysis of the gas.

Automatic correction to N.T.P. Various instruments have been devised with the object of eliminating the above calculations of a volume of gas to N.T.P. One of the best known is **Lunge's gas volumeter**: this is particularly useful where a large number of volume measurements have to be made as, for example, in the measurement of the volume of gas evolved from a weighed quantity of solid or liquid. The device is capable, however, of general application. The apparatus is shown in Fig. 6-7. **A** is the graduated tube in which the gas is to be measured, **B** is the " control " or " compensation " tube which has a spherical or cylindrical bulb at the upper end ; the volume to the first mark of the latter is 100 ml., the remaining narrow portion of the tube being calibrated up to 130 to 140 ml. in 0·1 ml. The " control " tube is set once for all at the beginning of the work by observing the temperature and pressure, and calculating the volume which 100 ml. of dry (or moist) air at N.T.P. would occupy under these conditions.* The " control " tube is then filled to the volume so calculated. If now the levelling tube **C** is adjusted so that the mercury in **B** is levelled on this 100 ml. mark, and the measuring tube **A** is adjusted so that the mercury levels in **A** and **B** are the same, the gas in **A** is under the same conditions of temperature and pressure as that in **B.** The reading on **B,** however, is known to represent the true volume of the gas in **B** corrected to N.T.P., hence the volume read on the graduated tube **A** will correctly represent the volume at N.T.P. **B** is kept dry or wet according as to whether the gas in **A** is dry or wet : the tubes are kept dry or wet by means of a drop of concentrated sulphuric acid or of water respectively. The instrument should be used in a room at uniform temperature,

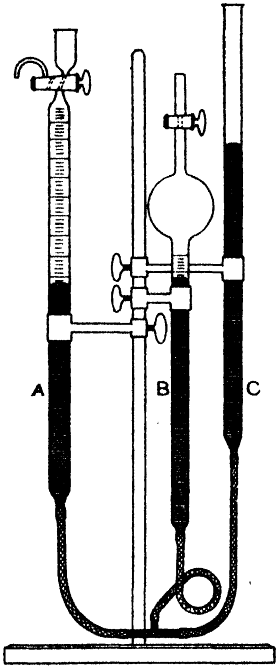

FIG. 6-7.

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* The necessary volumes V are given by the expressions :

$$\text{for dry gases} \quad V = \frac{100\,(273 + t)\,760}{273 \times P} ;$$

$$\text{for moist gases} \quad V = \frac{100\,(273 + t)\,760}{273 \times (P - p)} ,$$

where P is the atmospheric pressure expressed in mm. of mercury, t is the temperature in degrees Centigrade, and p is the vapour pressure of water in mm. of mercury at t°C.

and care must be taken to avoid heating one limb unequally either by contact with the hands or by unequal exposure to heat or draught. It may be mentioned that a difference of only 1°C would mean a variation of 0·3 per cent in the gas volume.

There are large numbers of automatic compensators, but for these the reader is referred to treatises on gas analysis.

VI, 5. Calibration of gas measuring vessels.—For work of only moderate precision the calibration of gas burettes, etc., is usually unnecessary, since instruments can be obtained with fairly accurate graduations. If, however, high accuracy is required, or the graduation is suspect, or the apparatus has been made or repaired in the laboratory, calibration must be carried out. Either the direct weighing method or that employing a " burette calibrator " (Section **II, 22**) may be used. The liquid employed in calibration should be the same liquid as is subsequently to be used in the burette, etc. In the majority of cases mercury is employed. A cathetometer is to be preferred for viewing the meniscus. The temperature of the mercury is, of course, noted, and the volume is calculated from the weight with the aid of Table XXV.

Meniscus correction. Gas burettes are usually calibrated inverted (see Fig. 6-8). If we consider the calibration of the burette in Fig. 6-8 (*a*) with mercury (which forms a convex meniscus), the volume desired is up to the plane **CD** ; it is evident that the volume of mercury weighed did not include the space **AEC** and **BED**. Moreover since the instrument is to be used in the reverse position, the error is really twice as great as is clear by inspection of Fig. 6-8 (*b*). This is called the **double meniscus correction,** and will obviously depend upon the internal diameter of the tube : the correction will be positive. If water is used in the burette for analysis and calibration purposes, the meniscus is concave upwards, and the correction instead of being

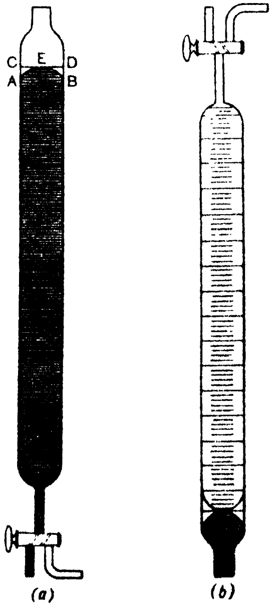

FIG. 6-8.

positive, as in the case of mercury, will be negative. Table XXVII, due to Göckel (1903), gives the values for the double meniscus correction with mercury and water respectively for tubes of various diameters.

TABLE XXVII. DOUBLE MENISCUS CORRECTION FOR WATER AND MERCURY.

Diameter of tube	*Double meniscus correction, ml.*		*Diameter of tube*	*Double meniscus correction, ml.*	
mm.	*Mercury*	*Water*	*mm.*	*Mercury*	*Water*
1	0·0026	0·0021	14	0·118	0·291
2	0·0052	0·0043	15	0·140	0·343
3	0·0090	0·0093	16	0·162	0·395
4	0·0128	0·0144	17	0·174	0·443
5	0·0200	0·026	18	0·185	0·492
6	0·027	0·039	19	0·181	0·520
7	0·035	0·062	20	0·177	0·548
8	0·043	0·084	21	0·180	0·605
9	0·056	0·114	22	0·182	0·663
10	0·068	0·144	23	0·179	0·708
11	0·080	0·190	24	0·176	0·754
12	0·091	0·236	25	0·173	0·800
13	0·104	0·263			

VI, 6. Apparatus employed in gas analysis.—Numerous forms of apparatus have been designed for gas analysis, and all that can be attempted in this Section is to give a brief account of the construction of only a few typical forms of apparatus.

A. Hempel's apparatus. This apparatus was formerly extensively employed for analyses of an accuracy of about 0·5 per cent. It consists of two parts, the burette, which includes a measuring tube and a levelling tube, and the pipette. The gas is usually measured over water or some aqueous solution.

The **Hempel-Winckler gas-burette** consists of two glass tubes mounted on feet, one tube being graduated to 100 ml. in 0·2 ml. (the burette proper) and the other plain (the pressure tube). They are connected at the feet by a long rubber tube as in Fig. 6-9.

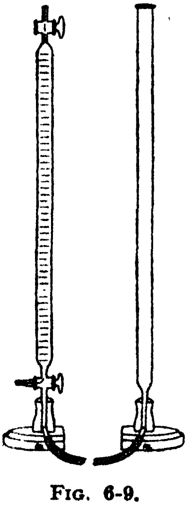

FIG. 6-9.

Here the burette is shown with a 2-way tap at the upper end and a 3-way tap at the lower end (this is the Winckler modification of the original Hempel burette, and must be employed for gases which are soluble in water). The **original Hempel burette** contained no glass taps, but was closed by a pinch-cock on a rubber tube at the upper end (this is shown in Fig. 6-17 in connexion with the method of manipulation); the upper end consists of a capillary tube of 1 mm. internal and 6 mm. external diameter. The glass tap burette is, however, more convenient in practice and more accurate.

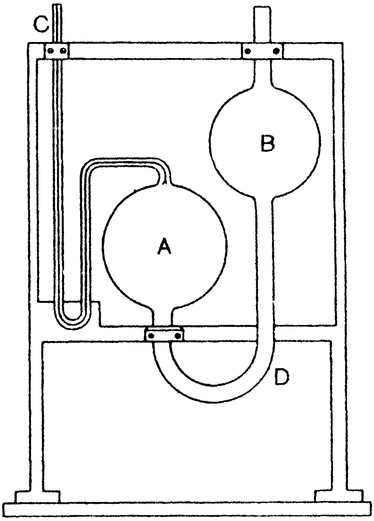

Fig. 6-10.

A **simple Hempel gas pipette** is shown in Fig. 6-10. This consists of two large bulbs **A** and **B** joined by the tube **D**; **C** is a capillary U-tube of 1 mm. internal diameter and about 6 mm. external diameter. Bulb **A** holds about 150 ml. and bulb **B** about 100 ml., so that when 100 ml. of gas is brought into **A**, sufficient space for the absorbing liquid will remain. The pipette is securely fastened to a wooden or iron stand; an iron stand with a four-sided base is generally preferable to wood because (i) its greater weight renders the apparatus more stable and (ii) it cannot warp. This pipette is employed for submitting the gas originally present in the burette to the action of a special liquid absorbent. The bulb **A** is filled with the absorbent liquid by pouring the latter into **B** and then sucking the air out of the apparatus at the capillary **C**; the liquid should reach the siphon bend of the capillary tube and bulb **B** should be nearly empty. It is convenient to keep a number of these pipettes filled with various absorbents (see Section **VI, 7**), well corked (or closed by rubber " policemen ") and labelled with the date on which fresh reagent was introduced. On each occasion that the pipette is used, the fact is noted on the label ; in this way it is possible to know approximately when it is necessary to recharge the apparatus.

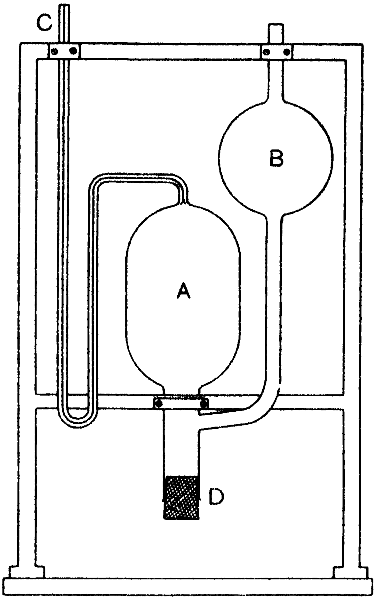

FIG. 6-11.

A **pipette** suitable **for solid (and liquid) reagents,** such as phosphorus in water, is shown in Fig. 6-11. The solid reagent is introduced through **D,** which is then closed with a rubber stopper and securely wired into place. This pipette is also useful for liquid reagents (*e.g.*, potassium hydroxide for carbon dioxide determinations) for it may be filled with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent ; the gas is thus exposed to a larger surface of the reagent and absorption is more rapid.

For solutions which undergo change upon exposure to the air, such as an alkaline solution of pyrogallol or an ammoniacal solution of cuprous chloride, the **double absorption pipette** (Fig. 6-12) is employed. Here the reagent in **B** is in contact with an atmosphere free from oxygen, the indifferent gas being confined over water in the bulbs **C** and **D.** This pipette is filled as follows. Tube **E** is first closed with a rubber stopper, and the apparatus is filled with

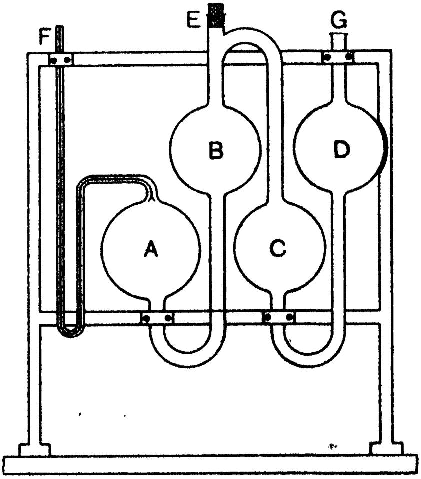

FIG. 6-12.

hydrogen or nitrogen by passing the gas through it. The reagent is introduced by pouring it through the tube **E,** and air-free water in through **G** until the bulb **C** is almost full—in order to form a water seal. The tube **E** is then closed by a rubber stopper, and wired on.

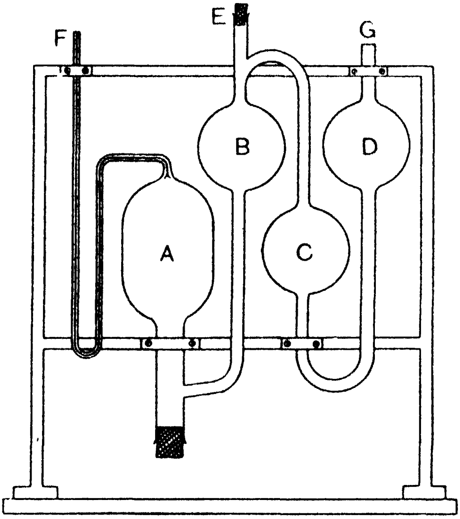

FIG. 6-13.

Fig. 6-13 is a **double absorption pipette** but adapted **for use with a solid (or liquid) absorbent.**

Fig. 6-14 shows the **simple absorption pipette used for fuming sulphuric acid.** This has an upper small bulb, about 5 cm. in diameter, filled with glass beads or broken glass in order to increase the absorbing surface. The ends of this pipette are closed when not in use by small glass caps, which can be made air-tight with rubber bands; a considerable improvement is effected by the use of ground-glass caps.

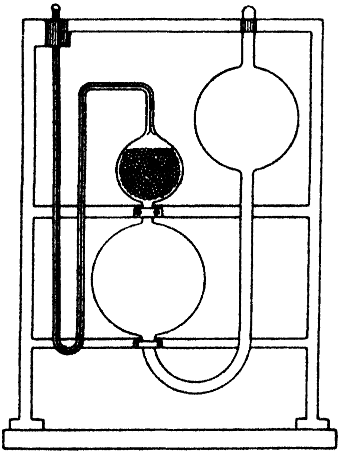

FIG. 6-14.

Fig. 6-15 depicts a **Hempel explosion pipette** : this contains mercury instead of water. A **slow combustion pipette** is illustrated in Fig. 6-16. The latter consists of a Hempel pipette for solid reagents with iron (or nichrome) electrodes inserted through the tubulature ; the electrodes terminate in a platinum spiral **P**, which is heated by a current of 2 to 3 amps. at 6 volts

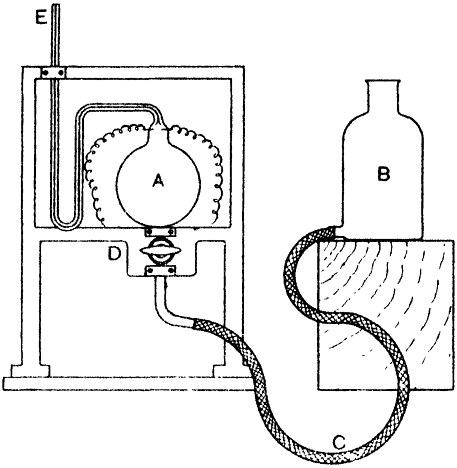

FIG. 6-15.

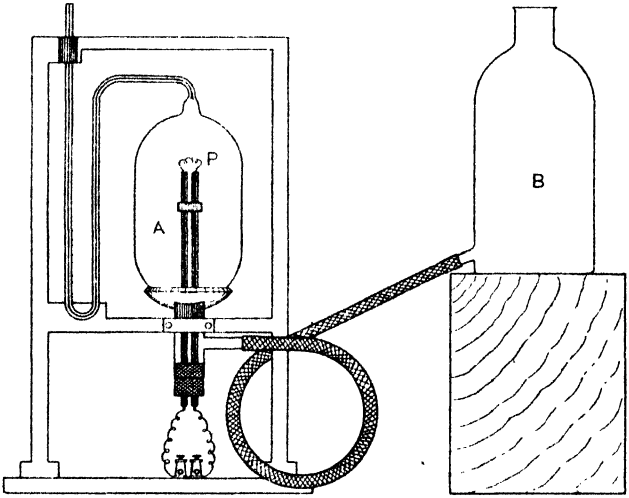

FIG. 6-16.

Manipulation of the Hempel apparatus. The complete apparatus is shown in Fig. 6-17. The experimental details for a simple Hempel burette (with pinch-cock) will be given ; the student should have no difficulty in modifying these to the use of the Hempel-Winckler burette. It is recommended that the pinch-clamp at **E** be of the Day type,* as this is far superior to the simple pinch-cock usually employed with burettes. If the burette has been in use, clean it thoroughly in the usual manner (Section **II, 19**), and rinse it well with distilled water. Make sure that the thick rubber tubing (" pressure tubing ") joint at the upper end of the burette is securely wired.† Open the pinch-clamp at **E,** and slip it down over the capillary tube. Pour water that has been saturated with the gas mixture to be analysed into the burette until **A** and **B** are rather more than half full. Drive out all the air from the rubber tubing connecting **A** and **B** by raising and lowering the tubes alternately, keeping the rubber tubing taut during the process. Raise **A** until the water begins to flow out of the top of **B,** then close the rubber tube of the burette with the pinch-clamp, which is placed close to the end of the capillary. Compress the rubber tubing at **C** between the thumb and fingers of the left hand, and pour out the excess of water that is in **A.**

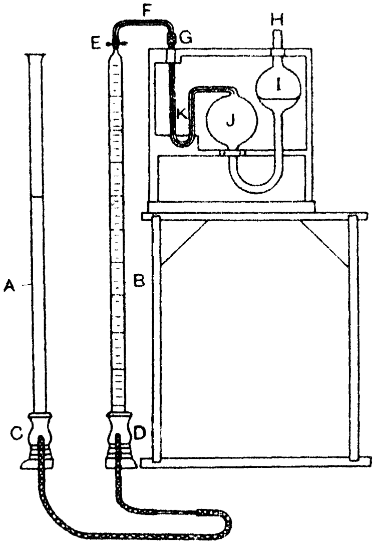

Fig. 6-17.

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* Supplied by the Central Scientific Co., Chicago, Ill., U.S.A., and also by E. H. Sargent and Co., 155-165 East Superior Street, Chicago, Ill., U.S.A.

† When joining together glass tubes by rubber tubing, the ends of the tubes should be rounded off in the flame, and then brought close together within the piece of rubber tubing. The rubber tubing is secured in place by means of wire ligatures, composed of copper wire about 1 to 2 mm. in diameter. Each ligature should consist of only one turn of the wire around the tube, the ends being drawn and tightly twisted together by means of a pair of pliers. Long rubber connexions should be avoided, not only because the rubber tubing is somewhat porous, but also because air in the tube tends to adhere tenaciously to the walls.

The next step is to measure out exactly 100 ml. of the gas sample. Insert into the rubber tube at **E** a capillary tube connected with the supply of the gas to be analysed, after first displacing the air in this connecting capillary by the gas. Hold the upper part of **A** in the left hand, lower it below **B**, and open the pinch-clamp **E** with the right hand. Introduce somewhat more than 100 ml. of gas into the burette. Close the pinch-cock **E**, level **A** and **B**, and allow the water in the burette to drain for 2 minutes. Disconnect the capillary tube from the source of gas, and adjust the volume of the gas by suitably manipulating the pinch-clamp until it is exactly 100 ml. when the levels of the liquids in the two tubes are the same.

The next stage is the absorption of one of the gaseous components of the mixture. Connect the burette and absorption pipette exactly as in Fig. 6-17 : the burette and level tube should be on a flat table. Insert into the rubber tubing **G** the bent capillary tube **F**. This connecting capillary has the same dimensions as the capillary tubes of the burette and pipette, *viz.*, 6 mm. external and 1 mm. internal diameter ; the horizontal portion is about 6 cm. long and the legs each about 2·5 cm. long. Slip a long piece of rubber tubing over the tube **H** of the pipette. Grasp **F** between the thumb and fingers of the right hand, squeeze the rubber tube **E** on the capillary tube of the burette between the thumb and fingers of the left hand, blow gently through **H** until the liquid in the pipette is driven over to a mark on the farther end of the horizontal portion of the capillary tube **F**, and then insert the end of **F** into the rubber tube on the burette. If the connexion is properly made, there will be practically no movement of the reagent in the capillary. Even if the air enclosed in the connexion between the burette and pipette should occupy about 1 cm. length of the capillary, the error may be neglected since capillary tubing of about 1 mm. bore occupies only about 0·01 ml. per cm. length. If, however, more than 1 cm. length of air remains in **F**, **F** should be slipped out of **E** and the operation repeated.* The apparatus is now ready for the absorption of a gas.

Open the pinch-clamp **E**, and slowly raise the levelling tube

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* Certain reagents must never be allowed to come into contact with the rubber connexion at **G** ; in such cases, the liquid from the pipette is forced upwards until it stands just below this rubber connexion and allowance is made for the air remaining in the capillary tubes. The correction is readily made since 10 cm. of the 1 mm. bore capillary corresponds to 0·1 ml. of air.

A, thus driving the gas over into the pipette. Allow the water to flow into the capillary tube **F** until it reaches the point to which the reagent has been driven over, and then close the pinch-clamp. A thin layer of the reagent adheres to the walls of the capillary, and this is sufficient to remove most of the absorbable constituent of the gas mixture remaining in the capillary. With some gases (*e.g.*, carbon dioxide) absorption occurs rapidly in the pipette, but with others (*e.g.*, oxygen and carbon monoxide) it is necessary to shake the pipette after the gas has been transferred into it. In the latter case, place another pinch-clamp on **G,** hold the burette in the left hand and gently rock the pipette stand backward and forward on the front edge of the base. After the constituent that is to be removed is completely absorbed, the gas is transferred back into the burette. This is done by holding the levelling tube in the left hand and in such a position that the confining liquid in it stands at a slightly lower level than in the burette, open pinch-clamp **E** (and, if necessary, that at **G**) and lower the levelling tube slowly until the gas is drawn back into the burette and the liquid in the pipette reaches a point on **F** at which it originally stood ; close the pinch-clamp **E**, level approximately, allow the water to drain for 2 minutes, level accurately, and take the reading of the volume of the gas in the burette. Absorption may not be complete in one operation. It is therefore advisable to transfer the gas back to the absorption pipette and to repeat the process until no further diminution in volume occurs.

By the use of a series of Hempel pipettes the gas is subjected to the action of various absorbents, one after another, until the complete composition is ascertained. As already pointed out, the connexions must in all cases be made with stout rubber tubing (" pressure " tubing) which are secured with copper wire ligatures.

For gases which are appreciably soluble in water, the levelling tube containing water cannot, of course, be used. The clean burette, which must be of the Hempel-Winckler type, is first thoroughly dried by washing it successively with alcohol and ether (alternatively by acetone alone) and then drawing air through it. The dry burette is filled with the gas either by the pressure of the gas or by using an aspirator bottle attached to the 3-way tap to draw out the air and replace it with the gas ; when the burette is full, the taps are turned off, care being taken that the gas is at atmospheric pressure. Connexion may then be made with the levelling tube **A**, which is then filled with water, the lower tap opened so that the water flows into the burette and absorbs the soluble gases present. As the burette holds exactly 100 ml. between the 3-way tap and the upper tap, the percentage of soluble gas can be read off directly.

The manipulation of the Hempel apparatus may be considerably simplified by utilising a special Hempel burette as shown in Fig. 6-18, and extending the capillary tube of the pipette so that it has a horizontal arm. The burette has a special 3-way tap with capillary tube arms; only one rubber connexion is required for attachment to the pipette.

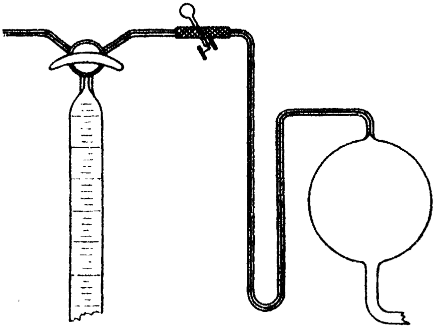

FIG. 6-18.

Attention is directed to the fact that the Hempel apparatus has been modified for the exact analysis of gaseous mixtures chiefly by (*a*) the use of a special burette with a device for automatically compensating for variations in temperature and barometric pressure, and (*b*) by the use of mercury as the confining liquid; the latter necessitates that the bulb **B** (see Fig. 6-10) is attached by means of " pressure " tubing to the bulb in which the actual absorption takes place.* It is doubtful whether such apparatus now finds a wide use because of the introduction of other more convenient apparatus for precision gas analysis (see below).

B. Bunte's apparatus. The apparatus is shown in Fig. 6-19 (*a*). The absorbent is introduced directly into the apparatus, and absorption takes place in the measuring vessel itself. Analyses are only of a second order accuracy, but the apparatus is of great value for the preliminary training of large classes of students in gas manipulation.

The **Bunte burette,** in an improved form, has a capacity of 100 ml. from the zero graduation to the upper 3-way tap, and is also graduated downwards from zero to 10 to 15 ml. for measuring the absorbing solution, if desired. In one form the tube is of uniform bore and is graduated in 0·2 ml. divisions ; in another form (not shown in the Figure) there is an upper bulb (capacity 50 ml.) graduated in 1 ml. divisions, and the lower half of the apparatus (50 ml. + 10-15 ml.) is the ordinary cylindrical tube graduated in 0·2 ml. **C** is a small cup-shaped vessel, which is somewhat over 25 ml. in capacity, and is provided with a 25 ml. (and sometimes also a 20 ml.) graduation mark. For more accurate results, the burette is surrounded by a water jacket, but this is ordinarily omitted. The capillary below **B** may be connected by means of rubber tubing to a levelling reservoir or bottle containing water ; this is adjustable to any height and is supported on a

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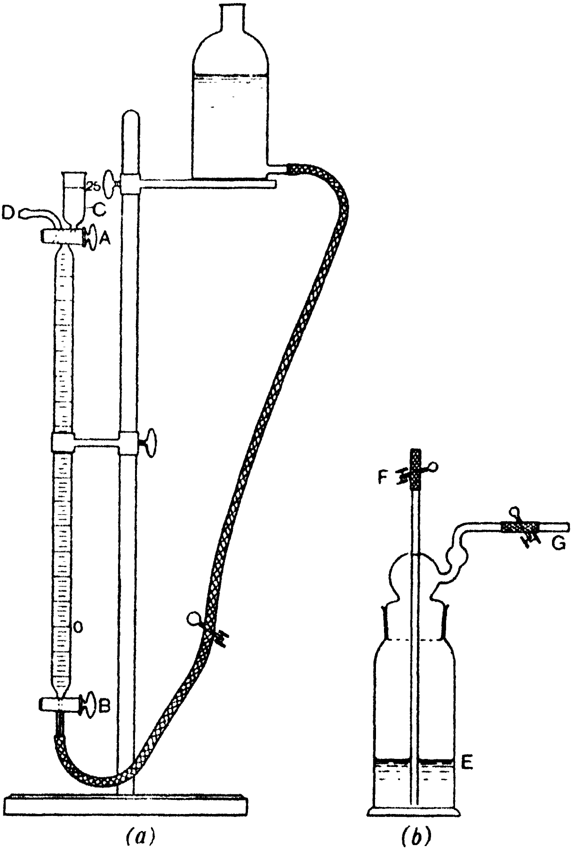
* For further details, see L. M. Dennis and M. L. Nichols, *Gas Analysis*, 1929 (The Macmillan Co.); G. W. Himus, *Fuel Testing*, 1932 (Leonard Hill).



(a) (b)

FIG. 6-19.

small circular platform fitted to a tall burette stand. Fig. 6-19 (*b*) is a gas wash bottle, fitted with short lengths of " pressure " tubing at **F** and **G**, which can be closed by means of screw clips or pinch-clamps.

Manipulation of the apparatus. Fill the levelling bottle, preferably saturated with the gas to be analysed, and connect it to the burette below **B**. Open taps **B** and **A**, and allow the water to run up to the upper mark in the cup **C**. Connect the stop-cock **A** through **D** to the supply of the gas, open **B**, lower the levelling bottle, turn tap **A** to the proper position and draw 101 to 103 ml. of the gas into the burette, and close tap **A**. Raise the levelling bottle, and compress the gas until the water exactly reaches the zero mark on the burette ; close tap **B**, open tap **A** cautiously so that the excess of gas bubbles through the water in the cup. The gas in the burette is now under atmospheric pressure plus the pressure of the water in the cup **C** ; these conditions must be reproduced in all subsequent measurements. Place a screw clip or pinch-clamp on the rubber tubing connecting the burette to the levelling bottle, and pull off the end of the tubing attached to the burette.

Almost fill the wash bottle, Fig. 6-19 (*b*), with water. Blow up the water into the rubber tube **F**, and close it with a screw clip. Attach the upper end of **F** to the lower end of the Bunte burette. Open tap **B**, and connect the wash bottle to a filter pump (at **G**) : open the screw clip at **G**, and suck the water in the burette until it is just above the tap **B**, which is then closed. The gas is now under less than atmospheric pressure, and when the tip of the burette is dipped under the absorbent in a shallow dish and the tap **B** opened, the absorbent will rise in the burette. Disconnect the wash bottle, place the end of the burette below the surface of a suitable absorbent contained in a shallow dish, and allow a suitable volume to enter ; then close tap **B**. Hold the burette above the upper tap and below the lower tap (to prevent heating of the gas), and shake well for a few minutes. Dip the tip of the burette under the absorbent, open tap **B**, and allow a little more of the absorbing solution to enter. Repeat the process until no more of the absorbent is sucked up into the burette. Empty most of the water from the wash bottle, and arrange so that water is contained only in the central tube and the rubber tubing **F**. Attach the water bottle to the lower end of the burette and connect **G** to a filter pump ;

suck out the absorbent from the burette until the absorbent just reaches tap **B**, and then close the tap. Dip the end of the burette into a dish containing water, which then rises in the tube. Close tap **B**, open tap **A** so that water flows into the burette from the cup **C** until the original pressure is produced. Add more water until it stands at the upper mark in the cup, and open tap **A** cautiously to reproduce the original pressure. Read the volume of the residual gas : the difference in volume gives the concentration directly in percentage by volume of the constituent absorbed.

The Bunte burette may be employed *inter alia* for the determination of carbon dioxide (by aqueous potassium hydroxide), heavy hydrocarbons (by bromine water), oxygen (by an alkaline solution if pyrogallol or, better, by alkaline sodium hyposulphite solution), and carbon monoxide (by ammoniacal cuprous chloride solution).

C. Orsat's apparatus. This apparatus, introduced by Orsat in 1874 and since modified by numerous workers, is widely used where an accuracy of about 0·5 per cent suffices, *e.g.*, for furnace gas analysis. The method of analysis is essentially similar to that with the Hempel apparatus, but the burette, pipettes and accessories are so designed that the whole apparatus, including three or four absorption pipettes, fit into a portable box.

The **Orsat-Lunge apparatus** is shown in Fig. 6-20. It consists of a water-jacketed burette of 100 ml. capacity, attached by means of a capillary tube manifold to four pipettes, three of which contain absorbents for carbon dioxide, oxygen and carbon monoxide respectively and which are usually filled with glass tubes or rods to present a greater surface of the reagent to the gas ; the fourth pipette contains water only and is used in conjunction with a tube containing purified asbestos impregnated with palladium and heated by means of a small spirit lamp. The last pipette and palladium-asbestos tube is omitted in some forms of the apparatus. The burette and reservoir to which it is attached contain acidulated water coloured with a suitable indicator, so that an indication is given at once of any accidental fouling with reagents. The gas mixture is drawn into the apparatus through the filter shown on the outside of the case (the filter may be dispensed with when working with gases free from dust) and through the 3-way stop-cock. If the gas to be sampled is at less than atmospheric pressure, the sampling tubes and filter are filled with gas by operation of a rubber aspirator (not shown in the figure) before the stop-cock is

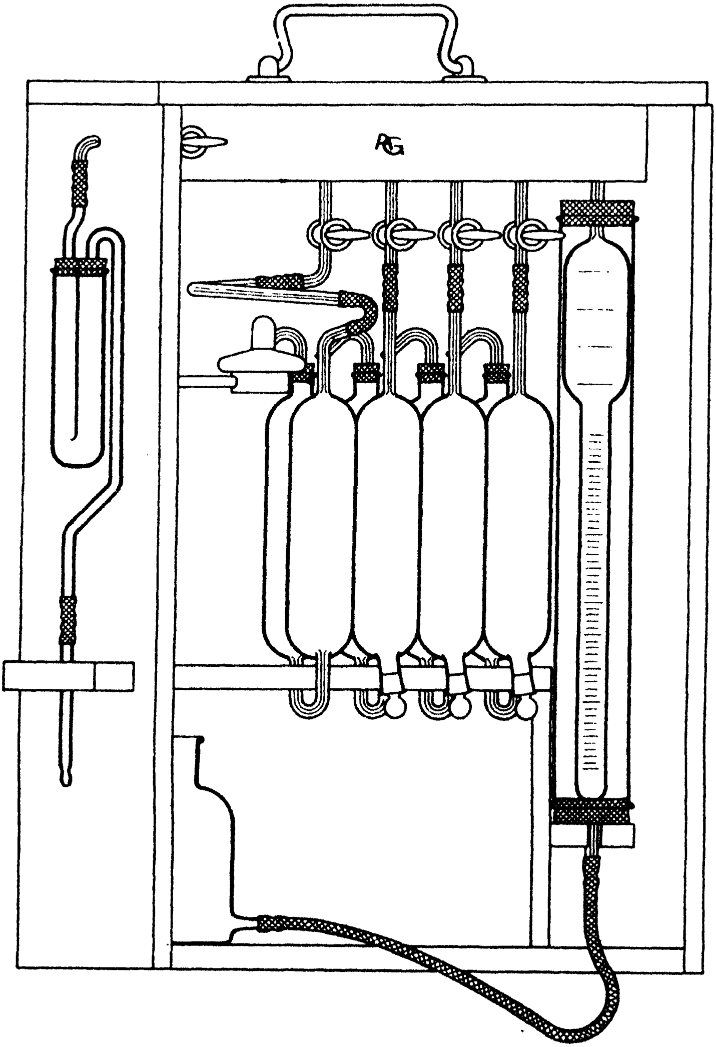


FIG. 6-20.

connected with the measuring burette. The first sample of gas drawn into the burette is discarded, it being employed to expel the air from the capillary connecting tubes. The reagent in each pipette is adjusted to a standard line just below the rubber connection, and under no circumstances must any of the reagent be drawn above the tap.

The method of carrying out the absorptions for carbon dioxide, oxygen and carbon monoxide is obvious (it is similar to that employed with the Hempel apparatus), and need not be further described. For the determination of hydrogen, which must be carried out after the above gases have been removed from the gaseous mixture, air is allowed to enter the burette until the total volume is approximately 100 ml. and the exact volume is read. The small capillary containing palladinised asbestos (situated at the left of the bulb containing water) is gently heated by means of a small spirit lamp, and the gas is passed very slowly from the burette into the pipette : the hydrogen will combine with the oxygen at the surface of the catalyst. The gas is returned to the burette and the process repeated, after which the volume of the residual gas is measured. Two-thirds of the contraction represents the volume of hydrogen. If the temperature is not allowed to rise above 200°, the volume of any methane and its homologues present which is burnt may be neglected in technical analyses. Various improvements for the determination of hydrogen and methane, either alone or in admixture, have been introduced. The most important of these are (i) a Pyrex U-tube containing cupric oxide and which can be heated in a small electric furnace at 270° to 300°C (**fractional combustion "pipette"**), and (ii) a pipette provided with a platinum wire spiral which can be heated electrically and its temperature controlled by a rheostat (**slow combustion pipette**). The fractional combustion pipette is employed to oxidise both carbon monoxide and hydrogen : at 270° to 300°C the oxidation may be effected in the presence of saturated hydrocarbons, such as methane and ethane (compare Section **VI, 8**). The diminution in volume gives the volume of hydrogen directly, whilst the combustion of carbon monoxide produces an equal volume of carbon dioxide ($2CO + O_2 = 2CO_2$), which can be determined by absorption ; in the latter case mercury must be employed as the confining liquid. As a general rule in the analysis of mixtures containing methane and ethane, it is best to determine the carbon monoxide by absorption and the hydrogen by fractional combustion over cupric oxide at about 290°C. The gas is passed through the copper oxide U-tube maintained at 290° to 300°C at a rate of 10 ml. per minute and back into the measuring vessel, and the process is repeated until there is no further contraction, The slow combustion pipette with, preferably, mercury as the confining liquid is employed for the determination of methane and/or ethane. A commercial form of portable apparatus is available which incorporates absorption pipettes of improved design, a fractional combustion " pipette," and a slow combustion pipette* ; this apparatus can therefore be employed for the determination of carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen, methane, ethane, and nitrogen (by difference).

A serious drawback of the Orsat-Lunge and similar apparatus is that the absorption of oxygen and carbon monoxide is not complete unless the absorbent and gas are shaken together or unless the gas is brought into prolonged and intimate contact with the absorbent. Shaking is, of course, not very practicable with this apparatus ; however, the use of pipettes packed with glass tubes considerably improves the absorption, but is nevertheless not quite satisfactory. Various improvements in the design of pipettes have been introduced, for example, by Dennis (spiral type)† and by others‡, but perhaps the best of these is due to M. Shepherd (1930). The latter is shown in Fig. 6-21** and is of the bubbling type the gas passes through a capillary tube, at the lower end of which is a platinum gas distributing disc (containing about 200 individual minute perforations) is sealed. The gas is thoroughly atomised, intimate contact is thus ensured, and absorption is complete.

The Orsat apparatus has been so modified and improved by M. Shepherd (1931) that it may be employed as a precision instrument for the analysis of gaseous mixtures. Mercury is employed as the confining liquid. The **Shepherd apparatus** in Pyrex glass is available commercially§ ; for further details

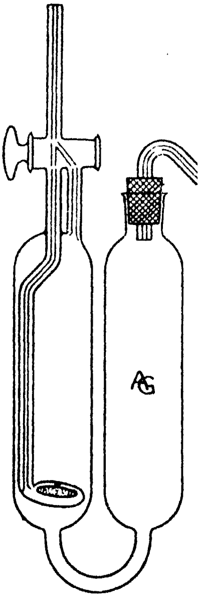


FIG. 6-21.

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* This is the " Fisher " gas analyser, technical universal model ; made by the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.

† L. M. Dennis and M. L. Nichols, *Gas Analysis*, 1929, p. 76.

‡ See the apparatus catalogues of the Fisher Scientific Co., E. H. Sargent and Company, Baird and Tatlock (London) Ltd., A. Gallenkamp and Co. Ltd., etc.

** Manufactured by the Fisher Scientific Co., Pennysylvania, Pa., U.S.A.

§ Supplied by E. H. Sargent and Co., Chicago, Ill., U.S.A.

the reader is referred to the booklet supplied by the manufacturers and also to the original memoir in the *Journal of Research of the Bureau of Standards* (1931, **6**, 121-127).

D. Ambler's portable apparatus. The apparatus, designed by H. R. Ambler (1931), is portable (the size complete in case is 15 × 12 × 4·5 inches and the weight is 8·5 lbs.), inexpensive, and can be used either for precision work or for routine determinations.* Mercury is employed as the confining liquid. The instrument is eminently suitable for the training of students in gas analysis.

The chief details of the apparatus are shown in Fig. 6-22, whilst Fig. 6-23 is a line diagram of the actual apparatus. Essentially the apparatus consists of (i) a 10 ml. burette **A**, surrounded by a water jacket, in which the gas is measured, (ii) a vessel **B** in which the gases are absorbed or combusted, and (iii) a graduated mercury manometer **M**. **A** and **B** are connected to mercury reservoirs $\mathbf{R}_1$ and $\mathbf{R}_2$ respectively ; $\mathbf{T}_1$ and $\mathbf{T}_2$ are 3-way and 2-way taps respectively ; reference marks are etched at **F** and **K** ; **B** contains a thin platinum coil, made from 1·5 cm. of platinum wire of 1·25 mm. diameter, and current is obtained from a 4·5 volt dry battery which is fixed on the base of the instrument and is controlled by a 3-ohm rheostat of the wireless component type ; the reservoir $\mathbf{R}_1$ is provided with two rests (shown in Fig. 6-23) at levels near the top and bottom of the manometer scale.

The general mode of use of the apparatus is as follows :

1. Introduce the gas sample (up to 10 ml.) into the vessel **B** by means of the capillary tube **H**, the tap $\mathbf{T}_1$ and the reservoir $\mathbf{R}_2$.

2. Reverse the tap $\mathbf{T}_1$, and transfer the gas to the measuring vessel **A**. Run the mercury to the mark **K**, and thus seal the gas in the burette.

3. Introduce a quantity of the appropriate absorbent into **B** from **H** by suitably manipulating $\mathbf{T}_1$ and $\mathbf{R}_2$.

4. Transfer the gas to **B** with the aid of $\mathbf{R}_1$ and $\mathbf{T}_2$. Absorption will take place.

5. Transfer the residual gas back into the measuring burette **A** by raising $\mathbf{R}_2$ and suitably turning $\mathbf{T}_1$. As soon as the absorbent liquid has reached the left-hand side of the tap $\mathbf{T}_1$, reverse the latter, and drive out the reagent through **H**.

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* The apparatus, and also a "works model" (with manometer omitted), is supplied by A. Gallenkamp and Co. Ltd., Sun Street, London, E.C.2, England.

Then reverse the tap, and adjust the mercury to the mark **K** as before.

The method of measurement of the gas varies according as to whether precision results (within 0·1 per cent) or moderately accurate ("technical," *i.e.*, within 0·5 per cent) are required. The measuring vessel consists of a burette of 10 ml. capacity, calibrated in 0·1 ml. Below the 10 ml. mark the burette narrows to a bore of 3 mm., and a mark **F** is etched round the lower part. Either varying volumes or varying pressures may be measured; the temperature is assumed constant, but may be corrected for if variations occur. The constant volume method is the more accurate. Three procedures will be described.

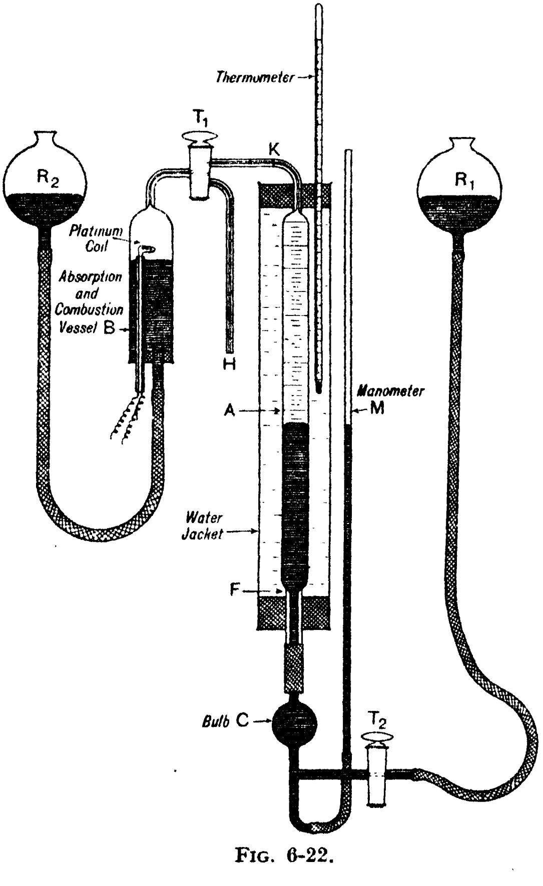

FIG. 6-22.

(*a*) *Varying volume and constant pressure.* This is the quickest procedure and yields results of " technical " accuracy. Level the mercury in the burette with the mercury in $\mathbf{R}_1$, which is held in the hand, and read the volume.

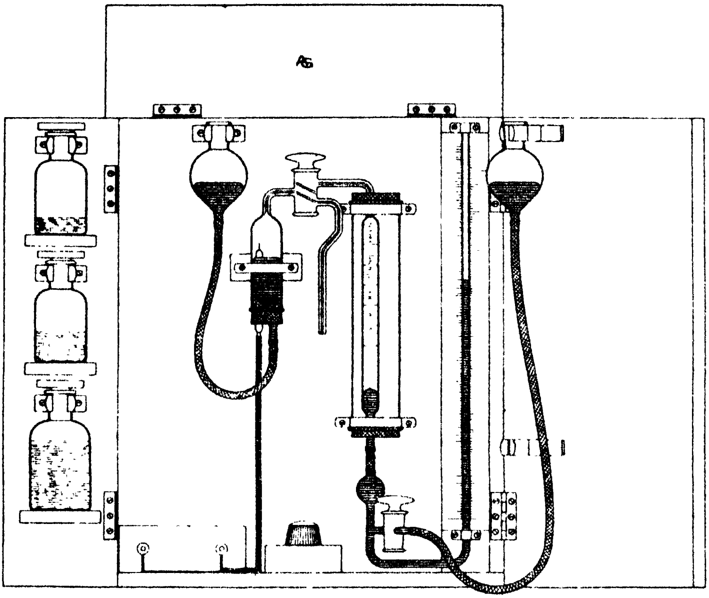

FIG. 6-23.

(*b*) *Varying volume and approximately constant pressure* (*corrected*). This modification of the constant pressure method is the most satisfactory for precision work. Bring the gas in the burette to approximately atmospheric pressure (say, to within 2 mm.), close the tap $\mathbf{T}_2$, and read both the burette and manometer. The pressure in the burette is then equal to the atmospheric pressure, plus the difference between the manometer reading and the reading of the manometer when the burette is filled to the same mark at atmospheric pressure. Let us call this difference ΔP.

The manometer readings corresponding with the different burette readings at atmospheric pressure are a constant of the apparatus, and are determined once and for all by measuring a few points with the tap $\mathbf{T}_1$ removed. These are plotted in the form of a graph, which is a straight line.

The correction to the burette reading is applied as follows. Let P be the atmospheric pressure, p the vapour pressure of water, V the burette reading (*i.e.*, the volume of moist gas at the experimental pressure), and V_a what the burette reading would have been if the mercury has been levelled to exactly atmospheric pressure. Then :

$$V_a = V \times \frac{P - p + \Delta P,}{P - p}$$

or
$$V_a - V = V \times \frac{\Delta P.}{P - p.}$$

If ΔP is not greater than 1 cm., then any deviation of $P - p$ from the average approximate figure $(76 - 1) = 75$ cm. will not affect the correction sufficiently to introduce an error of more than 0·1 per cent on the total gas. In practice, ΔP does not exceed 2 mm ; the magnitude of the correction, for 1 mm. of ΔP, is :

$$V \times (0{\cdot}1/75) = V \times 0{\cdot}0013, \text{ i.e., } 0{\cdot}13 \text{ per cent of } V.$$

(*c*) *Varying pressure and constant volume.* Many gas samples which occur in practice do not involve corrections greater than about 30 per cent of the total gas ; for this purpose a manometer of 30 cm. length will suffice. In such cases the maximum accuracy is obtained by the constant volume method. A knowledge of the volume is not required, and the result will be independent of any errors in the graduation of the burette. The mark **F** serves as a levelling mark for this purpose, and the bulb below the water jacket enables a sufficient volume of gas to be taken in the measuring burette at atmospheric pressure to be compressed to *ca.* 10·5 ml. (volume to mark **F**) at about 100 cm. pressure. It can be shown that the volume of the gas (at normal pressure) contained in the burette is proportional to :

$$P + A - K - p / 76,$$

where A is the manometer reading and K is the manometer reading with the burette at atmospheric pressure (all pressures are expressed in cm. of mercury).

Any other graduation may, of course, be employed, as in the case of samples which are not large enough to fill the burette. The precision then is somewhat less, since any error in levelling in the wider tube causes a greater error in volume.

Mention must be made of the fact that the vessel **B** may be fitted either with a spark gap or with a platinum spiral for the burning of hydrogen and other combustible gases ; the platinum spiral is of greater general utility. Gas mixtures containing more than 10 per cent of hydrogen or 3 per cent of hydrocarbons should be diluted with air before combustion.

The apparatus is applicable to all gases commonly dealt with. It can be used equally well for precise general analysis and for rapid technical analysis, and the volume of the sample required is small (normally 10 ml.). The use of mercury as the confining liquid increases the speed of transference of the gas, and determinations are correspondingly rapid.

E. Bone and Wheeler apparatus. This, in its simple or one of its modified forms, is probably the most widely used instrument for exact analysis in Great Britain, and is applicable to most classes of gaseous mixtures. The usual form of **Bone-Wheeler apparatus** is shown in Fig. 6-24. The gas mixture is measured at *constant volume* in limb **A** of the water-jacketed *U*-tube, the pressure being measured by the height of the mercury column in the limb **B,** which is graduated upwards in millimetres. The limb **A** has a series of graduations coinciding in level with each integral 100 mm. mark on **B.** The heights of **A** and **B** are such, that when a measurement is being made, the closed space above the mercury in **B** is a Torricellian vacuum except for water vapour; both limbs are kept saturated with water by means of a small quantity of dilute sulphuric acid (2 to 5 per cent). The pressure of the gas in **A** is equal to the difference in the level of the mercury

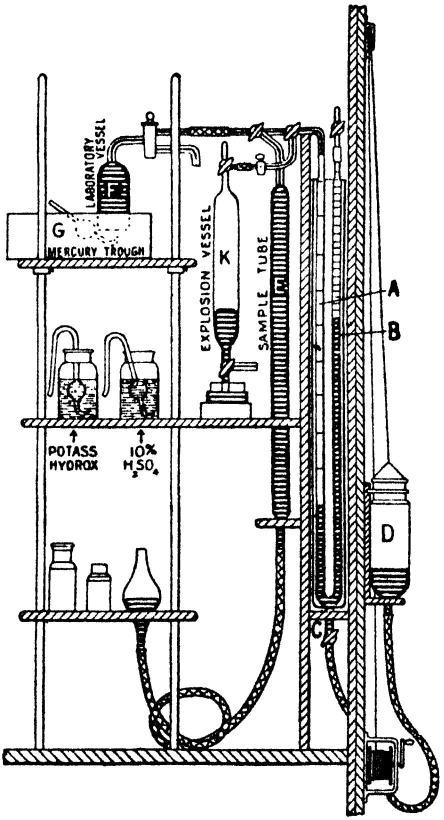

FIG. 6-24.

in **B** and **A**. Variations in the atmospheric pressure during the analysis do not affect the results, but variations in tem-

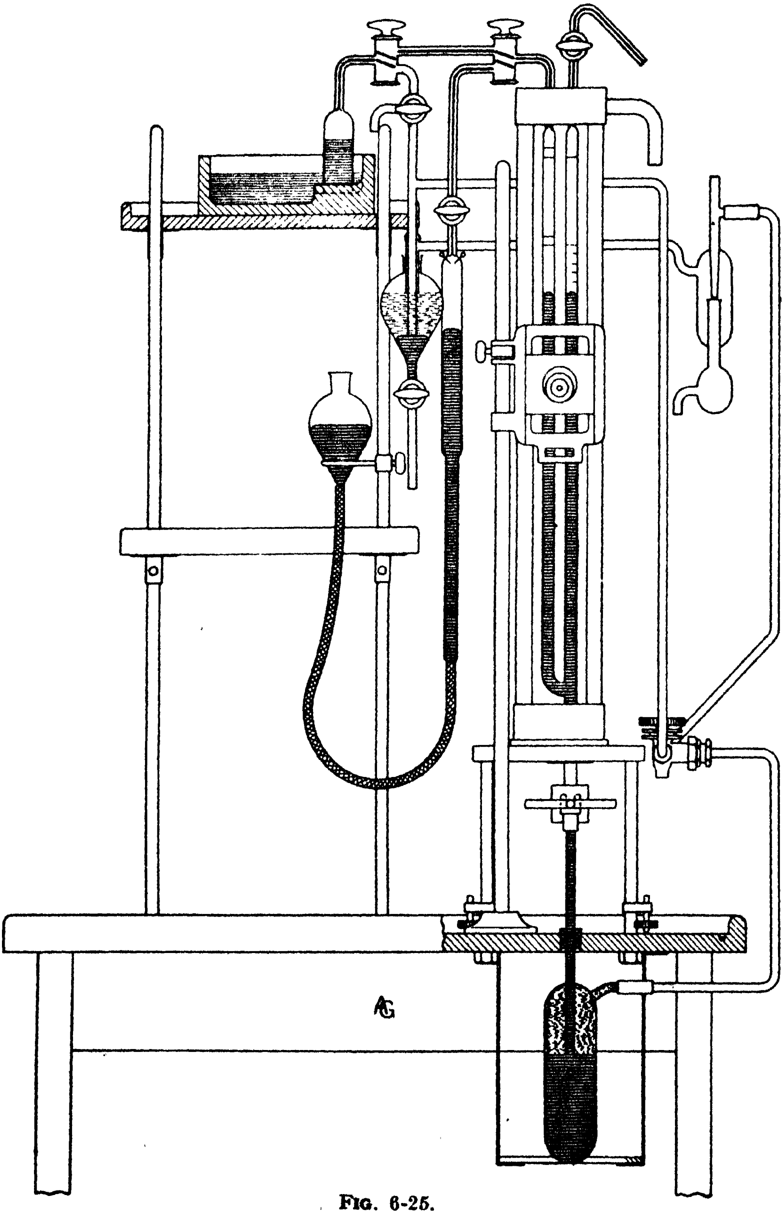

FIG. 6-25.

perature do affect the readings and corrections must be calculated (see Section **VI, 4**). Mercury is raised or lowered by means of the reservoir **D**, which is connected to a windlass and ratchet ; fine adjustments in levelling on to the marks is obtained by means of a special tap **C**, which separates the limbs **A** and **B** from **D**.

Absorption is carried out in the vessel (or pipette) **F**, which stands in a mercury trough ; the capillary 3-way tap at the top connects to the measuring vessel and to a bottle or other container connected to a filter pump or other exhausting apparatus, by means of which the reagent, introduced into **F** by means of a special bent pipette, may be removed after absorption has taken place. Combustible gases are determined by explosion with air in the vessel **K**, which is provided with a spark gap.*

Various modifications have been introduced, notably by J. G. King (1922) who incorporated a copper oxide tube for combustions,† and by Bone and Newitt (1929). The **Bone and Newitt apparatus** is shown in Fig. 6-25‡ ; the chief distinctive feature is the provision of a 3-way water tap of special design, by means of which the mercury levels are controlled from the water supply with ease and delicacy. The levels are read with a cathetometer. Otherwise, the procedure is similar to that with the Bone and Wheeler apparatus.**

A precision apparatus which permits of the analysis of 10 ml. of gas with an accuracy of ± 0·02 per cent has been described by B. Lambert and D. J. Borgars (Phil. Trans., 1939, **237**, 541-565).

F. Other precision forms of apparatus.—Most of these are of the " absorption pipette " type and employ mercury as the confining liquid. They are based upon the design originally introduced by Burrell and Oberfell (1916) and are often spoken of as U.S. Bureau of Mines apparatus. The Shepherd apparatus (Section **VI, 6C**) belongs to this class. Commercial forms of these gas analysers are marketed by several manufacturers.*

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* For further details, see G. Lunge-H. R. Ambler, *Technical Gas Analysis*, 1934 (Gurney and Jackson) ; A. McCulloch, *Gas Analysis*, 1938 (Witherby) ; F. Sutton-A. D. Mitchell, *Volumetric Analysis*, 1935 (Churchill).

† See the catalogues of Baird and Tatlock (London) Ltd., London and of A. Gallenkamp and Co. Ltd., London, England.

‡ Fig. 6-25 is reproduced by courtesy of A. Gallenkamp and Co. Ltd.

** For complete details of the manipulation of the apparatus, see G. W. Himus, *Fuel Testing*, 1932, p. 185 (Leonard Hill)

VI, 7. Absorbents for the various gases.—With all the types of apparatus described in the previous Section, the methods of determination of the constituent gases are essentially similar. The main sources of error by absorption methods are: (*a*) incomplete absorption due to insufficient time of contact, the use of an exhausted solution, or a chemical equilibrium between the gas and the compound formed by its action on the absorbent; (*b*) physical solution of constituent gases in reagents designed for the absorption of other constituents. The latter error is reduced to a minimum by the use of as small quantities of reagents as possible, and by saturating the reagents with the gases with which they come into contact: this is particularly necessary with instruments of the Hempel and Orsat type, where small volumes of reagents are not practicable.

The components of the gas mixture are usually determined in the **following order** by the methods detailed below.

A. Carbon dioxide. The most common reagent is a 25 to 33 per cent aqueous solution (by weight) of A.R. potassium hydroxide. For use in the Orsat apparatus a 40 to 50 per cent solution is recommended in order to reduce the number of times necessary to refill the apparatus. Sodium hydroxide should not be employed owing to the tendency of the bicarbonate to crystallise out; the potassium salt is much more soluble.

It will be appreciated that acid gases, such as hydrogen sulphide, sulphur dioxide and hydrogen cyanide, are also absorbed by the alkaline solution, and must be removed first.

B. Unsaturated hydrocarbons. The most satisfactory absorbent is fuming sulphuric acid, containing 20 to 25 per cent of free SO_3; the specific gravity is about 1·94. This absorbs all the olefines, acetylenes and aromatic hydrocarbons. The reagent must be employed at temperatures above 15°C, since below this temperature pyrosulphuric acid may crystallise out. Absorption is usually complete in 2 to 5 minutes; the rate of absorption is greatly accelerated by increasing the surface of the reagent by the use of glass rods or spheres (compare Fig. 6-14). The gas must be subsequently treated with potassium hydroxide solution to absorb acid vapours. Fuming sulphuric acid must not be kept for long periods over mercury, although it is quite safe to allow it to remain in contact with mercury for a few minutes, as in the Bone and Wheeler absorption pipette.

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* For further details, see, for example: (i) Dennis and Nichols, *Gas Analysis* (1929); (ii) the apparatus catalogues of E. H. Sargent and Co., Chicago, U.S.A., and of Fisher Scientific Co., Pittsburgh, Pa., U.S.A.; (iii) the booklet of the last-named firm entitled *Fisher Gas Analysis Manual* (revised edition).

A solution of bromine in 10 per cent potassium bromide solution is also employed to absorb unsaturated hydrocarbons. Bromine water attacks mercury much more readily than oleum, and is to be avoided, where possible, if mercury is used as the confining liquid for the gas. It is said (Himus, 1932) that the concentration may be so adjusted (to a deep yellow solution) that it absorbs effectively whilst having little action upon mercury. The gas must be washed subsequently with alkali to remove bromine vapour.

In technical practice the heavy hydrocarbons are usually absorbed together, but they may be absorbed separately by suitable means.

(i) Acetylene. This gas is absorbed by *ammoniacal cuprous chloride solution* with the formation of cuprous acetylide Cu_2C_2, but the reagent cannot be used in the presence of carbon monoxide and oxygen. With *potassium mercuric iodide reagent* only acetylene is absorbed and carbon monoxide is unaffected. The latter reagent (1 ml. absorbs 20 ml. of acetylene) is prepared by dissolving 25 g. of mercuric iodide and 30 g. of potassium iodide in 100 ml. of water, and mixing it with potassium hydroxide solution immediately before use.

(ii) Benzene. Benzene is readily absorbed by concentrated sulphuric acid, and can thus be separated from ethylene (which is not appreciably absorbed), but not from the higher olefines. Benzene may be removed by ammoniacal nickel cyanide reagent ; ethylene is not absorbed.

The **ammoniacal nickel cyanide reagent** is *prepared* as follows. Add a solution of 25 g. of potassium cyanide in 40 ml. of water to a solution of 50 g. of crystallised nickel sulphate in 75 ml. of water. Introduce 125 ml. of concentrated ammonia solution into the mixture, and shake until the nickel cyanide dissolves completely. Cool to 0°C, and allow to stand at this temperature for 20 minutes. Decant the clear liquid from the potassium sulphate that has separated, and treat with a solution of 18 g. of crystallised citric acid in 10 ml. of water. Allow the mixture to stand at 0°C for 10 minutes, decant the greenish-blue supernatant liquid, and transfer to the absorption pipette (*e.g.*, a Hempel double absorption pipette, Fig. 6-13, with the large bulb filled with broken glass). Add 2 drops of pure benzene to the reagent and shake the pipette until the benzene has combined with the reagent (2 to 3 minutes) ; this is shown by the appearance of fine, white, granular precipitate. The addition of a little benzene is necessary because it has been found that the freshly prepared reagent does not rapidly remove benzene vapour until some of the compound between benzene and the ammonium nickel cyanide has been formed.

C. Oxygen. The three absorbents which are commonly employed for the absorption of oxygen are a strongly alkaline solution of pyrogallol, a solution of sodium hyposulphite, and phosphorus respectively.

Alkaline pyrogallol. For the Orsat and Hempel type of apparatus a solution of 15 g. of pyrogallol in 100 ml. of 50 per cent aqueous potassium hydroxide (prepared from A.R., *i.e.*, electrolytic, KOH) is satisfactory. For the Ambler and Bone-Wheeler type of apparatus 40 per cent potassium hydroxide solution and 25 per cent aqueous pyrogallol solution are mixed in the ratio of 4 : 1 as required. At 20°C about 3 minutes' shaking is required for complete absorption; below 15°C absorption is inconveniently slow. With gases containing more than 25 per cent of oxygen, some carbon monoxide is always evolved, thus giving low results. A little carbon monoxide is also stated to be evolved with certain alkaline solutions of pyrogallol, but Haldane (1933) has shown that with the solution recommended above for the Orsat type of apparatus the effect is negligible if the solution is kept for 3 days before use or, alternatively, is heated at 100°C for an hour.

Sodium hyposulphite. The reaction which occurs is:

$$Na_2S_2O_4 + O_2 + H_2O = NaHSO_4 + NaHSO_3.$$

A suitable solution for general use is prepared by dissolving 50 g. of commercial sodium hyposulphite in 250 ml. of water, 30 g. of sodium hydroxide in 40 ml. of water, and mixing the solutions.* One ml. of this solution will absorb 10·5 ml. of oxygen. The absorption of oxygen is slower than with alkaline pyrogallol, but absorption also takes place at low temperatures at which the latter reagent is ineffective. Furthermore, no carbon monoxide is evolved or absorbed, and the reagent is unaffected by unsaturated hydrocarbons.

The rate of absorption can be considerably increased by the addition of *sodium anihraquinone-β-sulphonate.* Fieser (1924) recommends a solution of 16 g. of sodium hyposulphite, 6·6 g. of sodium hydroxide, 2 g. of sodium anthraquinone-β-sulphonate and 100 ml. of water. When this solution is exhausted, its colour changes from blood-red to brown; vigorous shaking is unnecessary. The reagent should not be kept for more than one week.

Solid phosphorus. Yellow phosphorus in the form of thin sticks may be employed for the absorption of oxygen in the Hempel pipette for solid reagents (Fig. 6-11) and in Orsat pipettes. A great advantage is that once a pipette has been charged with the reagent, it does not require renewing except after long periods. Absorption generally takes about 3 minutes: the oxygen content of the gas should not exceed 50 per cent, otherwise explosions may occur. During the absorption white clouds of oxide are produced and dissolve in the water: the clearing of these is a sign that absorption is complete. The water in which the phosphorus is immersed should be changed from time to time in order to remove the phosphoric and phosphorous acids which are formed. The phosphorus should be shielded from light, otherwise a layer of red phosphorus will be formed on the surface. The temperature should be above 15°C—below this temperature absorption is extremely slow. Even small quantities of acetylene and unsaturated hydrocarbons must be absent for these inhibit the reaction.

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* For use in the Bunte burette, a solution of 10 g. of $Na_2S_2O_4$ in 50 ml. of water mixed with 50 ml. of 10 per cent sodium hydroxide solution is preferable.

D. Carbon monoxide. The usual reagent for the absorption of carbon monoxide is **ammoniacal cuprous chloride solution**, which forms a complex $CuCl,2H_2O,CO$. The reagent may be prepared for use in the Ambler or Bone-Wheeler type of apparatus by adding 75 g. of white cuprous chloride to a solution of 15 g. of ammonium chloride in 80 ml. of water, and then adding sufficient concentrated ammonia solution until solution is complete. The solution should be kept in contact with copper wire or turnings in a stoppered bottle. For use in Hempel pipettes or in the Orsat type of apparatus, 125 ml. of concentrated hydrochloric acid are added to 40 g. of cuprous chloride in a suitable flask, followed by the cautious addition of 130 ml. of concentrated ammonia solution, the flask being cooled to atmospheric temperature: a little more ammonia solution (*ca.* 15 ml.) is then introduced until the white precipitate just dissolves.

The absorption of carbon monoxide by either of the above solutions is slow, and intimate contact between the gas and liquid is necessary. If the gaseous mixture contains more than 10 per cent of carbon monoxide, it should be treated a second time with a fresh solution. After the absorption ammonia must be removed from the gas by washing with water or with dilute sulphuric acid. Oxygen, acetylene and to some extent, ethylenes are absorbed by the reagent, and must previously be removed as already described.

A better reagent is **cuprous sulphate-β-naphthol**, with which a stable compound $Cu_2SO_4,2CO$ is formed. The **reagent** is *prepared* by cautiously adding 200 ml. of concentrated sulphuric acid, specific gravity 1·84, to 25 ml. of water ; the cool solution is added a little at a time to 20 g. of specially prepared cuprous oxide contained in a mortar, and the mixture is well ground to obtain the solid in fine suspension. 25 Grams of pure β-naphthol is added and incorporated in the mixture by grinding ; the final mixture is filtered through glass wool or *through a sintered glass funnel, and at once transferred to the absorption pipette. The reagent must be maintained above* 15°C and protected from the atmosphere ; the β-naphthol separates out at a lower temperature, and the mixture slowly oxidises if exposed to the atmosphere.

The **cuprous oxide** is *prepared* as follows. 100 Grams of cupric acetate are added to 1 litre of distilled water contained in a 2-litre flask, and the mixture heated until the acetate is dissolved. The solution is filtered, heated to the boiling point, treated with a solution of 60 g. of glucose in 400 ml. of water, the boiling continued until the blue colour fades somewhat, and the mixture allowed to stand until the red cuprous oxide separates out. The cuprous oxide is washed several times with water by decantation, transferred to a filter, washed once with alcohol, and finally dried in a vacuum desiccator.

The cuprous sulphate-β-naphthol reagent absorbs carbon monoxide completely (1 ml. absorbs *ca.* 5 ml. of CO), but not hydrogen or methane ; it is, however, rather slow in action and absorption may take up to 30 minutes. The gas should be washed with potassium hydroxide solution after contact with the reagent, since traces of acid fumes are liable to be produced.

E. Hydrogen. Hydrogen is usually determined, together with methane, etc., by combustion (Section **VI, 8**). However, in some cases it may be desirable to determine the gas by absorption.

The chief absorbent is palladium. If hydrogen is brought into contact with palladium in the presence of oxygen, the hydrogen is removed partly by absorption and partly by catalytic combustion. Two-thirds of the contraction is equal to the volume of hydrogen present. The method is far from accurate since any carbon monoxide and methane present may be partly oxidised too. If palladinised asbestos at 100°C is used, for example, in the Orsat apparatus (Section **VI, 6C**), the percentage of carbon monoxide and methane burnt will be small, and an *approximate* value for the hydrogen content may be obtained ; in technical analysis this value is corrected by determining the carbon dioxide simultaneously produced and adding this value to the initial contraction observed—a procedure which is open to many objections. The most satisfactory results are obtainable with a fractional combustion " pipette " (see Section **VI, 6C**).

VI, 8. Determination by explosion and combustion methods. —The most important gases determined by combustion methods are hydrogen, carbon monoxide, and saturated hydrocarbons (methane CH_4, ethane C_2H_6, etc.). The combustion *of these gases with excess of oxygen supplies three results, from which it is possible to determine the amount of gas burned and, in simple cases, its identity. The observa*tions which can be made are :

(i) Contraction in volume, v_1.

(ii) Volume of carbon dioxide produced, v_2 (determined by absorption in alkali after the combustion).

(iii) Volume of oxygen consumed, v_3 (determined by absorption after the removal of the carbon dioxide).

In the following table, the volume changes for a number of simple gases are shown ; these refer to *one* volume of the combustible gas.

	v_1	v_2	v_3
Hydrogen, H_2	3/2	0	1/2
Carbon monoxide, CO	1/2	1	1/2
Methane, CH_4	2	1	2
Ethane, C_2H_6	5/2	2	7/2
Paraffin, C_nH_{2n+2}	$(n + 3)/2$	n	$(3n + 1)/2$
Ethylene, C_2H_4	2	2	3
Olefine, C_nH_{2n}	$(n/2) + 1$	n	$3n/2$

The various equations from which the above table is derived are obvious and include the following for the commonly encountered gases :

$$\begin{aligned} 2H_2 &+ O_2 = 2H_2O\,; \\ 2CO &+ O_2 = 2CO_2\,; \\ CH_4 &+ 2O_2 = CO_2 + 2H_2O. \end{aligned}$$

Methods of effecting the combustion. A. Explosion. After the removal of such gases as are determined by absorption, excess of air or oxygen is added to the residue and the gas transferred to the explosion vessel, which is usually fitted with a platinum wire spark gap ; the spark is produced by an induction coil or by a magneto. The **Hempel explosion pipette** is shown in Fig. 6-15. It consists of a thick-walled explosion bulb **A** and the levelling vessel **B** which are connected by means of thick-walled rubber tubing (" pressure " tubing) and securely wired on. Two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. The pipette is filled with mercury. The gas to be determined together with excess of air or oxygen is transferred to the bulb **A,** the mixture brought approximately to atmospheric pressure, and the stop-cock **D** closed. The rubber tube attached to the extremity of **E** is next closed with a pinch-clamp, and the rubber tube closed by a suitable glass rod plug (which acts as a safety valve). The pipette is shaken to ensure complete mixture of the gases, a safety screen of thick plate glass (preferably of the " triplex " variety) placed in front of the pipette, and a few sparks passed (or until the gas is seen to explode). The tap **D** is immediately opened, the gas in the pipette transferred without delay to the burette, and is measured at once if the burette is filled with mercury or after 2 minutes if the burette contains water. The technique for explosion in a Bone-Wheeler or similar apparatus is self-evident from the above description.

The chief source of error or failure in explosion analysis is an incorrect proportion of the combustible gas in the explosive mixture. If the proportion is too low, explosion does not take place or is incomplete ; if it is too high and nitrogen is present, oxides of nitrogen are produced, giving excessive contractions and erroneous carbon dioxide figures. For hydrogen, the hydrogen content must be between 10 and 20 per cent ; for methane, the corresponding limits are 6·0 and 8·3 per cent ; for mixtures containing these gases, proportionately intermediate figures apply. The results for carbon monoxide by the explosion method (20 to 28 per cent) are not always satisfactory.

B. Slow combustion. Catalytic combustion with platinum. In the presence of oxygen, all combustible gases are oxidised in contact with platinum wire at about 950°C ; hydrogen and carbon monoxide are oxidised at a much lower temperature. The usual method of carrying out the combustion is by means of an electrically heated platinum wire. A **slow combustion pipette,** due to Dennis (1899), is shown in Fig. 6-16. It is really a Hempel pipette for solid absorbents (Fig. 6-11) into the neck of which a 2-holed rubber stopper is inserted which carries two glass tubes reaching to within 2 cm. of the top of the pipette. Stout iron (or nichrome) wires, 2·5 cm. in diameter, are mounted inside the tubes and reach nearly to the top ; the upper ends of the wires carry small iron screws to which a platinum wire spiral is attached, and the current passing through the spiral is controlled by a rheostat. The pipette and levelling tube contain mercury. In use, a known volume (excess) of oxygen is passed into the pipette followed by a known volume of the gas to be burned. With non-explosive gas mixtures, a current is passed through the platinum spiral, which is maintained at the requisite temperature with the aid of a rheostat, for 1 or 2 minutes. For hydrogen and carbon monoxide, one minute's treatment at a red heat is sufficient, but for methane, which is difficult to burn, 2 minutes at a bright yellow heat is usually required. After combustion, the current is turned off, the pipette allowed to cool, and the gas residue passed back into the burette and measured. The reader should be able to adapt the above experimental details for the Ambler and Bone-Wheeler type of apparatus.

An **improved combustion pipette,** due to Weaver and Ledig (1920) and to Shepherd (1931), is shown in Fig. 6-26. It is made of Pyrex glass, has a volume of approximately 150 ml., and is used with mercury as the confining liquid ; the lower end is attached by means of rubber tubing to a levelling bulb. This is incorporated in Shepherd's modification of the Orsat apparatus (see Section **VI, 6C**). About 20 cm. of wire (90% Pt and 10% Ir alloy) of 0·16 to 0·17 cm. diameter is employed in the construction of the coil; the side arms, through which the wire passes, are sealed with DeKhotinsky cement.

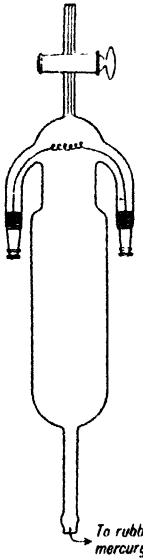

FIG. 6-26.

For mixtures which are liable to explode, and also to reduce the danger of explosion in any combustion process, the **combustion pipette of Ambler** (1931)—Fig. 6-27—is a valuable improvement upon the ordinary design. Oxygen is bubbled through the lower capillary tube side limb, thus enabling the rate of inflow to be seen and readily adjusted ; in this way the gaseous mixture, already present in the pipette, may be burned in a controlled stream of oxygen.

Combustion with copper oxide. Copper oxide at 270° to 295°C oxidises carbon monoxide and hydrogen rapidly and completely, methane and other hydrocarbons being unaffected. This is an example of fractional combustion and is utilised for separating these gases. The oxygen is supplied by the copper oxide; if oxygen is present, however, it acts as a catalyst and is not reduced.* Fractional combustion cannot be used in the presence of unsaturated hydrocarbons.

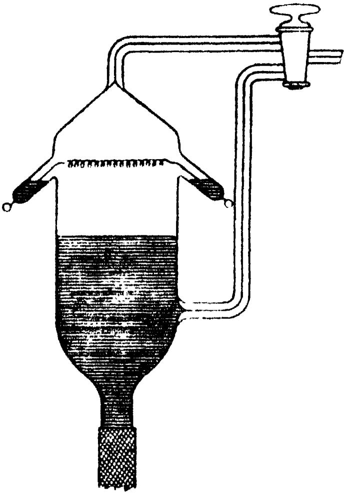

FIG. 6-27.

VI, 9. Exercises in gas analysis.—The exact nature of these will depend upon the apparatus and gaseous mixtures which are available, upon the particular interests of the teacher (and of the student), and upon local conditions. The following are suggested as suitable for classes of moderate size: they are likely to be useful in all laboratories as an introduction to gas analysis.

1. Determination of oxygen in air. A Winckler-Hempel burette, preferably filled with mercury and surrounded by a water jacket, and a Hempel pipette, filled with phosphorus or with sodium hyposulphite solution, may be used.

2. Analysis of coal gas by means of the Bunte burette. Determination of carbon dioxide with potassium hydroxide solution, heavy hydrocarbons with bromine water, oxygen with sodium hyposulphite solution, and carbon monoxide with ammoniacal cuprous chloride solution (for order of absorption, see Section **VI, 7**).

3. Analysis of coal gas by means of the Orsat apparatus. Absorbents as under *2*.

4. Analysis of coal gas with the Ambler portable apparatus. Absorbents as under *2*.

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* For further details, see Lunge-Ambler, *Technical Gas Analysis*, 1934, p. 141. The method is widely employed for the determination of hydrogen, and also of carbon monoxide if saturated hydrocarbons are absent.

A, 2. CHEMICAL FACTORS*

Sought	*Found*	*Factor*	*Log Factor*
Pb	$PbSO_4$	0·68325	$\bar{1}$·83458
	$PbCrO_4$	0·64108	$\bar{1}$·80691
	$PbMoO_4$	0·56436	$\bar{1}$·75156
	PbO_2	0·86623	$\bar{1}$·93763
Ag	AgCl	0·75263	$\bar{1}$·87658
Hg	HgS	0·86221	$\bar{1}$·93561
	$Hg[Zn(CNS)_4]$	0·40259	$\bar{1}$·60486
	$[Cu(C_4H_{16}N_4)][HgI_4]$	0·22488	$\bar{1}$·35195
Bi	BiOI	0·59388	$\bar{1}$·77370
	$Bi(C_6H_3O_3)$	0·62937	$\bar{1}$·79890
	Bi_2O_3	0·89700	$\bar{1}$·95279
	$Bi(C_9H_6ON)_3$	0·32583	$\bar{1}$·51299
Cd	$CdMoO_4$	0·41273	$\bar{1}$·61566
	$[(C_{13}H_9N)_2H_2]CdI_4$	0·11464	$\bar{1}$·05934
	$Cd(C_{10}H_6O_2N)_2$	0·24612	$\bar{1}$·39115
	$[Cd(C_5H_5N)_2](CNS)_2$	0·29065	$\bar{1}$·46336
Cu	$Cu_2(CNS)_2$	0·52257	$\bar{1}$·71814
	$Cu(C_{14}H_{11}O_2N)$	0·22011	$\bar{1}$·34264
	$Cu(C_7H_6O_2N)_2$	0·18930	$\bar{1}$·27715
	$Cu(C_{10}H_6O_2N)_2,H_2O$	0·14926	$\bar{1}$·17394
	$[Cu(C_5H_5N)_2](CNS)_2$	0·18812	$\bar{1}$·27444
	$[Cu(C_4H_{16}N_4)][HgI_4]$	0·07126	$\bar{2}$·85285
As	As_2S_3	0·60903	$\bar{1}$·78463
	$Mg(NH_4)AsO_4,6H_2O$	0·25887	$\bar{1}$·41309
	$Mg_2As_2O_7$	0·48258	$\bar{1}$·68356
	U_3O_8	0·26683	$\bar{1}$·42624
Sb	Sb_2S_3	0·71687	$\bar{1}$·85544
	Sb_2O_4	0·79189	$\bar{1}$·89866
	$Sb(C_6H_5O_4)$	0·46321	$\bar{1}$·66578
Sn	SnO_2	0·78766	$\bar{1}$·89634
Mo	$PbMoO_4$	0·26133	$\bar{1}$·41719
	MoO_3	0·66655	$\bar{1}$·82383
	$MoO_2(C_9H_6ON)_2$	0·23051	$\bar{1}$·36269
Te	TeO_2	0·79951	$\bar{1}$·90282

***For discussion on chemical factors, see Section IV, 3.**

CHEMICAL FACTORS—*Continued*

Sought	*Found*	*Factor*	*Log. Factor*
Pd	$Pd(C_4H_7O_2N_2)_2$	0·31669	$\bar{1}$·50064
	$Pd(C_{10}H_6O_2N)_2$	0·23658	$\bar{1}$·37398
	$Pd(C_{10}H_6O_3N)_2$	0·22091	$\bar{1}$·34421
Al	Al_2O_3	0·52913	$\bar{1}$·72357
	$Al(C_9H_6ON)_3$	0·05871	$\bar{2}$·76868
Be	BeO	0·36051	$\bar{1}$·55692
Cr	Cr_2O_3	0·68425	$\bar{1}$·83522
	$BaCrO_4$	0·20527	$\bar{1}$·31233
Fe	Fe_2O_3	0·69940	$\bar{1}$·84472
Ni	$Ni(C_4H_7O_2N_2)_2$	0·20314	$\bar{1}$·30780
	$Ni(C_7H_6O_2N)_2$	0·17734	$\bar{1}$·24881
	$[Ni(C_5H_5N)_4](CNS)_2$	0·11947	$\underline{1}$·07727
	$Ni(C_{14}H_{11}O_2N_2)_2$	0·10926	$\bar{1}$·03844
Co	$Co(C_{10}H_6O_2N)_3,2H_2O$	0·09640	$\bar{2}$·98406
	$Co(C_{10}H_6O_3N)_3$	0·09454	$\bar{2}$·97564
	$[Co(C_5H_5N)_4](CNS)_2$	0·11992	$\bar{1}$·07890
Zn	$Zn(NH_4)PO_4$	0·36648	$\bar{1}$·56405
	$Zn_2P_2O_7$	0·42912	$\bar{1}$·63257
	ZnS	0·67098	$\bar{1}$·82671
	$Zn(C_{10}H_6O_2N)_2,2H_2O$	0·14668	$\bar{1}$·16638
	$[Zn(C_5H_5N)_2](CNS)_2$	0·19245	$\bar{1}$·28431
Mn	$Mn_2P_2O_7$	0·38708	1·58780
U	U_3O_8	0·84802	$\bar{1}$·92841
UO_2	U_3O_8	0·96200	$\bar{1}$·98318
U	$UO_2(C_9H_6ON)_2,C_9H_7ON$	0·33840	$\bar{1}$·52943
Th	ThO_2	0·87884	$\bar{1}$·94391
Ce	CeO_2	0·81409	$\bar{1}$·91067
Ti	$TiO(C_9H_6ON)_2$	0·13601	$\bar{1}$·13356
	TiO_2	0·59950	$\bar{1}$·77779
Zr	$Zr_2P_2O_7$	0·51190	$\bar{1}$·70918
	ZrO_2	0·74030	$\bar{1}$·86941

CHEMICAL FACTORS—*Continued*

Sought	*Found*	*Factor*	*Log. Factor*
Tl	Tl_2CrO_4	0·77894	$\bar{1}$·89150
	$Tl_3[Co(NO_2)_6]$	0·64669	$\bar{1}$·81070
Ca	CaC_2O_4,H_2O	0·27430	$\bar{1}$·43822
	$CaCO_3$	0·40044	$\bar{1}$·60254
	CaO	0·71469	$\bar{1}$·85412
Sr	$SrSO_4$	0·47705	$\bar{1}$·67857
	SrO	0·84560	$\bar{1}$·92717
Ba	$BaSO_4$	0·58847	$\bar{1}$·76972
	$BaCrO_4$	0·54213	$\bar{1}$·73411
Mg	$Mg(C_9H_6ON)_2,2H_2O$	0·06976	$\bar{2}$·84359
	$Mg(C_9H_6ON)_2$	0·07780	$\bar{2}$·89096
	$Mg(NH_4)PO_4,6H_2O$	0·09909	$\bar{2}$·99602
	$Mg_2P_2O_7$	0·21851	$\bar{1}$·33947
Na	Na_2SO_4	0·32376	$\bar{1}$·51022
	$NaZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$	0·01495	$\bar{2}$·17475
	$NaMg(UO_2)_3(C_2H_3O_2)_9,6\cdot 5H_2O$	0·01274	$\bar{2}$·10500
K	$K_2[PtCl_6]$	0·16083	$\bar{1}$·20637
	$KClO_4$	0·28217	$\bar{1}$·45052
	K_2SO_4	0·44888	$\bar{1}$·65213
	$K_2Na[Co(NO_2)_6]H_2O$	0·17215	$\bar{1}$·23591
Li	Li_2SO_4	0·12625	$\bar{1}$·10123
	$LiCl$	0·16369	$\bar{1}$·21402
NH_4	$(NH_4)_2[PtCl_6]$	0·08125	$\bar{2}$·90983
W	WO_3	0·79303	$\bar{1}$·89929
	$WO_2(C_9H_6ON)_2$	0·36477	$\bar{1}$·56202
	Anions		
Cl	AgCl	0·24737	$\bar{1}$·39334
Br	AgBr	0·42555	$\bar{1}$·62895
I	AgI	0·54055	$\bar{1}$·73283
	PdI_2	0·70405	$\bar{1}$·84761

CHEMICAL FACTORS—*Continued*

Sought	*Found*	*Factor*	*Log Factor*
CNS	AgCNS $Cu_2(CNS)_2$ $BaSO_4$	0·34996 0·47744 0·24882	$\bar{1}$·54402 $\bar{1}$·67891 $\bar{1}$·39589
CN	AgCN	0·19413	$\bar{1}$·28850
F	PbClF CaF_2 $(C_6H_5)_3SnF$	0·07261 0·48668 0·05149	$\bar{2}$·86100 $\bar{1}$·68724 $\bar{2}$·71173
ClO_3	AgCl	0·58224	$\bar{1}$·76510
ClO_4	AgCl $KClO_4$	0·69387 0·71783	$\bar{1}$·84128 1·85602
SO_4	$BaSO_4$	0·41153	$\bar{1}$·61440
S	$BaSO_4$	0·13735	$\bar{1}$·13783
SO_3	$BaSO_4$	0·34299	$\bar{1}$·53528
S_2O_3	$BaSO_4$	0·24017	$\bar{1}$·38052
PO_4	$Mg_2P_2O_7$ $P_2O_5,24MoO_3$	0·85337 0·05281	$\bar{1}$·93114 $\bar{2}$·72275
HPO_3	Hg_2Cl_2 $Mg_2P_2P_7$	0·16942 0·71869	$\bar{1}$·22896 $\bar{1}$·85654
H_2PO_2	Hg_2Cl_2 $Mg_2P_2O_7$	0·06884 0·58401	$\bar{2}$·83781 $\bar{1}$·76642
C_2O_4	CaC_2O_4,H_2O $CaCO_3$ CaO	0·60238 0·87941 1·56954	$\bar{1}$·77987 $\bar{1}$·94419 0·19577
SiO_3	SiO_2	1·26640	0·10257
SiF_6	SiO_2	2·36530	0·37389
NO_3	$C_{20}H_{16}N_4,HNO_3$	0·16519	$\bar{1}$·21799

A, 3. THE LITERATURE OF ANALYTICAL CHEMISTRY

The following list is not intended to be exhaustive*; it indicates books and journals which may well form the nucleus of a library for analytical chemistry. A number of comparatively elementary works on general analysis are included because these contain references to the scientific literature.

1. Theory of Analytical Chemistry.

H. Bassett. *The Theory of Quantitative Analysis.* G. Routledge, 1925.
T. B. Smith. *Analytical Processes.* E. Arnold, 1929.

2. General Reference Works.

W. F. Hillebrand and G. E. F. Lundell. *Applied Inorganic Analysis.* J. Wiley; Chapman and Hall, 1929.
W. W. Scott and N. H. Furman. *Standard Methods of Chemical Analysis. Vol. I. The Elements.* 5th Edition. Van Nostrand; Technical Press, 1939.
J. W. Mellor and H. V. Thompson. *A Treatise on Quantitative Inorganic Analysis.* 2nd Edition. C. Griffin and Co., 1938.
G. E. F. Lundell and J. I. Hofmann. *Outline of Methods of Chemical Analysis.* J. Wiley; Chapman and Hall, 1938.
A. D. Mitchell and A. M. Ward. *Modern Methods in Quantitative Chemical Analysis.* Longmans, Green and Co., 1932.
C. A. Mitchell. *Recent Advances in Analytical Chemistry. Vol. II. Inorganic.* Churchill, 1931.

3. Text Books.

F. P. Treadwell-W. T. Hall. *Analytical Chemistry. Vol. II. Quantitative Analysis.* 8th Edition. J. Wiley; Chapman and Hall, 1935.
I. M. Kolthoff and E. B. Sandell. *Text Book of Quantitative Inorganic Analysis.* Macmillan, 1936.
H. H. Willard and N. H. Furman. *Elementary Quantitative Analysis.* 2nd Edition. Van Nostrand; Macmillan, 1935.
H. A. Fales. *Inorganic Quantitative Analysis.* Century, 1925.
W. D. Treadwell. *Tabellen und Vorschriften zur Quantitativen Analyse.* Franz Deuticke, 1938.

4. Volumetric Analysis.

F. Sutton-A. D. Mitchell. *A Systematic Handbook of Volumetric Analysis.* 12th Edition. Churchill, 1935.
W. Böttger-R. E. Oesper. *Newer Methods of Volumetric Analysis.* Van Nostrand; Chapman and Hall, 1938.
I. M. Kolthoff-N. H. Furman. *Volumetric Analysis.* 2 Vols. J. Wiley; Chapman and Hall, 1928–29.
G. S. Jamieson. *Volumetric Iodate Methods.* Chemical Catalog. Co., 1926.
E. Knecht and E. Hibbert. *New Reduction Methods in Volumetric Analysis.* 2nd Edition. Longmans, Green and Co., 1925.

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* A more detailed list of books is to be found in E. J. Crane and A. M. Patterson, *A Guide to the Literature of Chemistry* (J. Wiley, 1927) and in J. Olsen, *Van Nostrand's Chemical Annual* (1935).

5. Electro-analysis. Electrochemistry.

E. F. Smith. *Electro-analysis.* 6th Edition. Blakiston, 1919.

A. Classen and H. Danneel. *Quantitative Analyse durch Elektrolyse* 7th Edition. J. Springer, 1927.

A. Fischer-A. Schleicher. *Elektro-analytischer Schnellmethoden.* 2nd Edition. F. Enke, 1926.

W. Böttger. *Physikalische Methoden der analytischen Chemie.* Band II. Akad. Verlag, 1936.

H. J. S. Sand. *Electrochemistry and Electrochemical Analysis.* Blackie, 1940

S. Glasstone. *The Electrochemistry of Solutions.* 2nd Edition. Methuen, 1937.

D. A. MacInnes. *The Principles of Electrochemistry.* Reinhold Publishing Corporation ; Chapman and Hall, 1939.

N. A. McKenna. *Theoretical Electrochemistry.* Macmillan, 1939.

6. Gas Analysis.

L. M. Dennis and M. L. Nichols. *Gas Analysis.* Revised Edition. Macmillan, 1929.

G. Lunge-H. R. Ambler. *Technical Gas Analysis.* Revised Edition. Gurney and Jackson, 1934.

G. W. Himus. *Fuel Testing.* Leonard Hill, 1932.

J. S. Haldane and J. J. Graham. *Methods of Air Analysis.* 4th Edition C. Griffin and Co., 1935.

7. Colorimetric Analysis.

J. H. Yoe. *Photometric Chemical Analysis. Vol. I. Colorimetry. Vol. II. Nephelometry.* J. Wiley ; Chapman and Hall, 1928–29.

E. D. Snell and C. R. Snell. *Colorimetric Methods of Analysis. Vol. I. Inorganic.* Van Nostrand ; Chapman and Hall, 1936.

Absolutkolorimetrische Metallanalysen mit dem Pulfrich-Photometer. Carl Zeiss, Jena, 1938.

8. Electrometric Methods.

I. M. Kolthoff and N. H. Furman. *Potentiometric Titrations.* 2nd Edition. J. Wiley ; Chapman and Hall, 1931.

H. T. S. Britton. *Conductometric Analysis.* Chapman and Hall, 1934.

H. T. S. Britton. *Hydrogen Ions.* 2nd Edition. Chapman and Hall, 1932.

W. M. Clark. *The Determination of Hydrogen Ions.* 3rd Edition. William and Wilkins ; Bailliere, Tindall and Cox, 1928.

I. M. Kolthoff and N. H. Furman, *Colorimetric and Potentiometric Determination of* p*H*. J. Wiley ; Chapman and Hall, 1931.

9. Micro-analysis, Organic Reagents, etc.

F. Emich-F. Schneider. *Micro-chemical Laboratory Manual.* J. Wiley ; Chapman and Hall, 1932.

F. Pregl-H. Roth-E. B. Daw. *Quantitative Organic Micro-analysis.* Churchill, 1937.

J. R. Niederl and V. Niederl. *Micro-methods of Quantitative Organic Elementary Analysis.* J. Wiley ; Chapman and Hall, 1938.

E. M. Chamot and C. W. Mason. *Handbook of Chemical Microscopy.* Vol. I. 2nd Edition, 1938. Vol. II. 1st Edition, 1930. J. Wiley ; Chapman and Hall.

F. Feigl-J. W. Mathews. *Qualitative Analysis by Spot Tests.* Nordemann Publishing Co., 1937.

H. V. A. Briscoe and J. W. Mathews. *Micro-chemical Methods suitable for General Analytical Practice.* Institute of Chemistry, London, 1934.

E. M. Chamot. *Chemical Microscopy* (in Scott-Furman, Standard Methods of Chemical Analysis, Vol. II, p. 2435, 1939).

L. T. Hallett. *Quantitative Micro-chemical Analysis* (in Scott-Furman, Standard Methods of Chemical Analysis, Vol. II, p. 2460, 1939).

Organic Reagents for Metals. 3rd. Edition. Hopkin and Williams, London, 1938.

C. J. van Nieuwenburg, W. Böttger, F. Feigl, A. S. Komarovsky and N. Strafford. *Tables of Reagents for Inorganic Analysis* (Premier Rapport de la " Commission internationale des Réactions et Réactifs analytiques nouveaux " de l'" Union Internationale de Chimie," Paris). Akad Verlag, Leipzig ; H. K. Lewis, London, 1938.

10. Qualitative Analysis.

R. K. McAlpine and B. A. Soule. *Qualitative Chemical Analysis.* Van Nostrand ; Chapman and Hall, 1933.

A. I. Vogel. *A Text Book of Qualitative Chemical Analysis.* Longmans, Green and Co., 1937.

F. P. Treadwell-W. T. Hall. *Analytical Chemistry. Vol. I. Qualitative Analysis.* 9th Edition. J. Wiley ; Chapman and Hall, 1937.

A. A. Noyes and W. C. Bray. *A System of Qualitative Analysis for the Rarer Elements.* Macmillan, 1927.

11. Metallurgical Analysis.

G. E. F. Lundell, J. I. Hofmann and H. A. Bright. *Chemical Analysis of Iron and Steel.* J. Wiley ; Chapman and Hall, 1931.

W. A. Naish and J. E. Clennell. *Select Methods of Metallurgical Analysis.* Chapman and Hall, 1929.

N. W. Lord and D. J. Demorest. *Metallurgical Analysis.* 5th Edition. McGraw-Hill, 1924.

U.S. Steel Corporation. *Sampling and Analysis of Carbon and Alloy Steels.* Reinhold Publishing Corporation ; Chapman and Hall, 1938.

F. Ibbotson and L. Aitchison. *The Analysis of Non-Ferrous Alloys.* 2nd Edition. Longmans, Green and Co., 1922.

W. B. Price and R. K. Meade. *The Technical Analysis of Brass and Non-Ferrous Alloys.* J. Wiley ; Chapman and Hall, 1922.

E. Gregory and W. W. Stevenson. *Chemical Analysis of Metals and Alloys.* Blackie, 1937.

12. Ore Analysis.

A. H. Low. *Technical Methods of Ore Analysis.* 10th Edition. J. Wiley ; Chapman and Hall, 1936.

H. S. Washington. *Chemical Analysis of Rocks.* 4th Edition. J. Wiley ; Chapman and Hall, 1930.

W. R. Schoeller and A. R. Powell. *The Analysis of Minerals and Ores of the Rarer Elements.* C. Griffin and Co., 1919.

A. W. Groves. *Silicate Analysis.* T. Murby, 1938.

H. F. Harwood. *Analysis of Rocks and Minerals.* Annual Reports on the Progress of Chemistry, 1938, **34**, 464–480.

13. Water Analysis.

J. C. Thresh, J. F. Beale and E. V. Suckling. *The Examination of Water and Water Supplies.* Churchill, 1933.

W. P. Mason and A. M. Buswell. *Examination of Water.* 6th Edition. J. Wiley ; Chapman and Hall, 1931.

Standard Methods for the Examination of Water and Sewage. 8th Edition. American Public Health Association, 1936.

D. K. French. *Water Analysis* (in Scott-Furman, Standard Methods of Chemical Analysis, Vol. II, p. 2046 ; 1939).

14. Reagents.

" *Analar* " *Standards for Laboratory Chemicals.* 2nd Edition. Hopkin and Williams Ltd., London and British Drug Houses Ltd., London, 1937.

J. Rosin. *Reagent Chemicals and Standards.* Van Nostrand ; Chapman and Hall, 1937.

Reports of the Committee on Guaranteed (*or Analytical*) *Reagents of the American Chemical Society.* Ind. Eng. Chem., 1925, **17**, 756 ; 1926, **18**, 636, 759 ; 1927, **19**, 645, 1369 ; 1928, **20**, 979. Ind. Eng. Chem. Anal. Edn., 1929, **1**, 171 ; 1930, **2**, 351 ; 1931, **3**, 221 ; 1932, **4**, 154, 347 ; 1933, **5**, 289.

15. Cement.

R. K. Meade. *Portland Cement.* Chemical Publishing Co., 1926.

W. C. Hanna. *Cement* (in Scott-Furman, Standard Methods of Chemical Analysis, Vol. II, p. 1597 ; 1939).

16. General Industrial Analysis.

W. W. Scott-N. H. Furman. *Standard Methods of Chemical Analysis, Vol. II. Special Subjects.* 5th Edition. Van Nostrand-Technical Press, 1939.

G. Lunge-C. A. Keane-P. C. L. Thorne. *Technical Methods of Chemical Analysis.* 2nd Edition. 3 Vols. Gurney and Jackson, 1924–31.

A. H. Allen. *Commercial Organic Analysis.* 5th Edition. 8 Vols. Blakiston ; Churchill, 1923–30.

17. Agricultural Analysis, Food Analysis, etc.

W. W. Skinner *et al.* *Official and Tentative Methods of Analysis.* 4th Edition. Association of Official Agricultural Chemists, Washington, 1935.

E. G. Mahin and R. H. Carr. *Quantitative Agricultural Analysis.* McGraw-Hill, 1923.

C. H. Wright. *Agricultural Analysis.* T. Murby, 1938.

H. W. Wiley. *Principles and Practice of Agricultural Analysis. Vol. I. Soils.* 3rd Edition, 1926. *Vol. II. Fertilisers and Insecticides.* 3rd Edition, 1931. Chemical Publishing Co.

A. G. Woodman. *Food Analysis.* 3rd Edition. McGraw-Hill, 1931.

A. W. Blyth-M. W. Blyth-H. E. Cox. *Foods : Their Composition and Analysis.* 7th Edition. C. Griffin and Co., 1927.

H. E. Cox. *The Chemical Analysis of Foods.* 2nd Edition. Churchill, 1938.

C. G. Moor-W. Partridge-J. R. Nicholls. *Aids to the Analysis of Foods and Drugs.* 5th Edition. Baillière, Tindall and Cox, 1934.

C. K. Tinckler and H. Masters. *Applied Chemistry. Vol. I. Water Detergents, Fuels, Textiles, etc.* 3rd Edition, 1935. *Vol. II. Foods.* 2nd Edition, 1932. The Technical Press,

18. Apparatus, etc.

Much valuable information concerning apparatus is to be found in the catalogues of various manufacturers. A selected list is given below. Some firms publish booklets from time to time in which recent improvements of laboratory apparatus and technique are described.

A. Gallenkamp and Co. Ltd., 17-29 Sun Street, London, E.C.2, England.
Baird and Tatlock (London) Ltd., Cross Street, London, E.C.1, England.
Griffin and Tatlock Ltd., Kemble Street, London, W.C.2, England.
F. E. Becker and Co., Hatton Wall, London, E.C.1, England.
Fisher Scientific Co., 709–719 Forbes Street, Pittsburgh, Pa., U.S.A.
E. H. Sargent and Co., 155–165 East Superior Street, Chicago, U.S.A.
Central Scientific Co., 1700 Irving Park Blvd., Chicago, U.S.A.
Eimer and Amend, 205–223 Third Avenue, New York, N.Y., U.S.A.

Bulletin and Laboratory Notes, published by Baird & Tatlock (London) Ltd.
The Laboratory, published by the Fisher Scientific Co.
Cenco News Chats, published by the Central Scientific Co.
The Nivoc Supplement, published by F. E. Becker and Co.

Short pamphlets announcing new or improved apparatus are published from time to time by the other firms noted above.

19. Chemical and Physical Constants.

E. W. Washburn et al. *International Critical Tables*. 7 Vols. McGraw-Hill, 1926–30.
H. Landolt-R. Bornstein. *Physikalisch-Chemische Tabellen*. 5th Edition. J. Springer, 1923–36.
G. W. C. Kaye and T. H. Laby. *Tables of Physical and Chemical Constants*. 8th Edition. Longmans, Green and Co., 1936.
N. A. Lange. *Handbook of Chemistry*. 2nd Edition. Handbook Publishers, 1937.
C. D. Hodgman. *Handbook of Chemistry and Physics*. 20th Edition. Chemical Rubber Publishing Co., 1935.
J. C. Olsen. *Van Nostrand's Chemical Annual*. 7th Issue. Van Nostrand ; Chapman and Hall, 1935.
E. Hope. *The Chemists' Year Book*. Sherratt and Hughes, 1938.

20. Journals.

A list of the most important Journals in which the results of original research in analytical chemistry are published is given below. Many memoirs on chemical analysis appear in numerous other scientific journals ; abstracts of these may be found in the *British Chemical Abstracts* published by the Bureau of Chemical Abstracts, London, or in *Chemical Abstracts* published by the American Chemical Society. Valuable summaries appear in the *Annual Reports on the Progress of Chemistry* published by the Chemical Society, London.

The Analyst.
Industrial and Engineering Chemistry, Analytical Edition.
Annales de Chimie analytique et de Chimie appliquée et Revue de Chimie analytique réunies.
Zeitschrift für analytischen Chemie.
Journal of the Chemical Society.
Journal of the American Chemical Society.
Bulletin de la Societé chimique de France.
Berichte der deutschen chemischen Gesellschaft.
Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
Journal of Research of the National Bureau of Standards.

A, 4. DENSITIES OF ACIDS AT 20°C

(DENSITIES AND PERCENTAGES BY WEIGHT ARE BASED ON WEIGHTS IN VACUO, AND THE PERCENTAGE BY WEIGHT REFERS TO THE FORMULA GIVEN.)

Per Cent By Weight	*Density*				
	H_2SO_4	HNO_3	$H.C_2H_3O_2$	H_3PO_4	HCl
1	1·0051	1·0036	0·9996	1·0038	1·0032
2	1·0118	1·0091	1·0012	1·0092	1·0082
3	1·0184	1·0146	1·0025	—	—
4	1·0250	1·0201	1·0040	1·0200	1·0181
5	1·0317	1·0256	1·0055	—	—
6	1·0385	1·0312	1·0069	1·0309	1·0279
7	1·0453	1·0369	1·0083	—	—
8	1·0522	1·0427	1·0097	1·0420	1·0376
9	1·0591	1·0485	1·0111	—	—
10	1·0661	1·0543	1·0125	1·0532	1·0474
11	1·0731	1·0602	1·0139	—	—
12	1·0802	1·0661	1·0154	1·0647	1·0574
13	1·0874	1·0721	1·0168	—	—
14	1·0947	1·0781	1·0182	1·0764	1·0675
15	1·1020	1·0842	1·0195	—	—
16	1·1094	1·0903	1·0209	1·0884	1·0776
17	1·1168	1·0964	1·0223	—	—
18	1·1243	1·1026	1·0236	1·1008	1·0878
19	1·1318	1·1088	1·0250	—	—
20	1·1394	1·1150	1·0263	1·1134	1·0980
21	1·1471	1·1213	1·0276	—	—
22	1·1548	1·1276	1·0288	1·1263	1·1083
23	1·1626	1·1340	1·0301	—	—
24	1·1704	1·1404	1·0313	1·1395	1·1187
25	1·1783	1·1469	1·0326	—	—
26	1·1862	1·1534	1·0338	1·1529	1·1290
27	1·1942	1·1600	1·0349	—	—
28	1·2023	1·1666	1·0361	1·1665	1·1392
29	1·2104	1·1733	1·0372	—	—
30	1·2185	1·1800	1·0384	1·1805	1·1493
31	1·2267	1·1867	1·0395	—	—
32	1·2349	1·1934	1·0406	—	1·1593
33	1·2432	1·2002	1·0417	—	—
34	1·2515	1·2071	1·0428	—	1·1691
35	1·2599	1·2140	1·0438	1·216	—
36	1·2684	1·2205	1·0449	—	1·1789
37	1·2769	1·2270	1·0459	—	—
38	1·2855	1·2335	1·0469	—	1·1885
39	1·2941	1·2399	1·0479	—	—
40	1·3028	1·2463	1·0488	1·254	1·1980
41	1·3116	1·2527	1·0498	—	—
42	1·3205	1·2591	1·0507	—	—
43	1·3294	1·2655	1·0516	—	—
44	1·3384	1·2719	1·0525	—	—
45	1·3476	1·2783	1·0534	1·293	—
46	1·3569	1·2847	1·0542	—	—
47	1·3663	1·2911	1·0551	—	—
48	1·3758	1·2975	1·0559	—	—
49	1·3854	1·3040	1·0567	—	—
50	1·3951	1·3100	1·0575	1·335	—

DENSITIES OF ACIDS AT 20°C—*Continued*

Per Cent By Weight	*Density*			
	H_2SO_4	HNO_3	$H.C_2H_3O_2$	H_3PO_4
51	1·4049	1·3160	1·0582	—
52	1·4148	1·3219	1·0590	—
53	1·4248	1·3278	1·0597	—
54	1·4350	1·3336	1·0604	—
55	1·4453	1·3393	1·0611	1·379
56	1·4557	1·3449	1·0618	—
57	1·4662	1·3505	1·0624	—
58	1·4768	1·3560	1·0631	—
59	1·4875	1·3614	1·0637	—
60	1·4983	1·3667	1·0642	1·426
61	1·5091	1·3719	1·0648	—
62	1·5200	1·3769	1·0653	—
63	1·5310	1·3818	1·0658	—
64	1·5421	1·3866	1·0662	—
65	1·5533	1·3913	1·0666	1·475
66	1·5646	1·3959	1·0671	—
67	1·5760	1·4004	1·0675	—
68	1·5874	1·4048	1·0678	—
69	1·5989	1·4091	1·0682	—
70	1·6105	1·4134	1·0685	1·526
71	1·6221	1·4176	1·0687	—
72	1·6338	1·4218	1·0690	—
73	1·6456	1·4258	1·0693	—
74	1·6574	1·4298	1·0694	—
75	1·6692	1·4337	1·0696	1·579
76	1·6810	1·4375	1·0698	—
77	1·6927	1·4413	1·0699	—
78	1·7043	1·4450	1·0700	—
79	1·7158	1·4486	1·0700	—
80	1·7272	1·4521	1·0700	1·633
81	1·7383	1·4555	1·0699	—
82	1·7491	1·4589	1·0698	—
83	1·7594	1·4622	1·0696	—
84	1·7693	1·4655	1·0693	—
85	1·7786	1·4686	1·0689	1·689
86	1·7872	1·4716	1·0685	—
87	1·7951	1·4745	1·0680	—
88	1·8022	1·4773	1·0675	—
89	1·8087	1·4800	1·0668	—
90	1·8144	1·4826	1·0661	1·746
91	1·8195	1·4850	1·0652	—
92	1·8240	1·4873	1·0643	1·770
93	1·8279	1·4892	1·0632	—
94	1·8312	1·4912	1·0619	1·794
95	1·8337	1·4932	1·0605	—
96	1·8355	1·4952	1·0588	1·819
97	1·8364	1·4974	1·0570	—
98	1·8361	1·5008	1·0549	1·844
99	1·8342	1·5056	1·0524	—
100	1·8305	1·5129	1·0498	1·870

A, 5. DENSITIES OF ALKALINE SOLUTIONS AT 20°C

(Densities and Percentages by Weight are Based on Weights in Vacuo, and the Percentage by Weight refers to the Formula Given.)

Per Cent By Weight	*Density*			*Per Cent By Weight*	*Density*		
	KOH	$NaOH$	NH_3		KOH	$NaOH$	NH_3
1	1·0083	1·0095	0·9939	26	1·2489	1·2848	0·9040
2	1·0175	1·0207	0·9895	27	1·2592	—	—
3	1·0267	1·0318	—	28	1·2695	1·3064	0·8980
4	1·0359	1·0428	0·9811	29	1·2800	—	—
5	1·0452	1·0538	—	30	1·2905	1·3279	0·8920
6	1·0544	1·0648	0·9730	31	1·3010	—	—
7	1·0637	1·0758	—	32	1·3117	1·3490	—
8	1·0730	1·0869	0·9651	33	1·3224	—	—
9	1·0824	1·0979	—	34	1·3331	1·3696	—
10	1·0918	1·1089	0·9575	35	1·3440	—	—
11	1·1013	—	—	36	1·3549	1·3900	—
12	1·1108	1·1309	0·9501	37	1·3659	—	—
13	1·1203	—	—	38	1·3769	1·4101	—
14	1·1299	1·1530	0·9430	39	1·3879	—	—
15	1·1396	—	—	40	1·3991	1·4300	—
16	1·1493	1·1751	0·9362	41	1·4103	—	—
17	1·1590	—	—	42	1·4215	1·4494	—
18	1·1688	1·1972	0·9295	43	1·4329	—	—
19	1·1786	—	—	44	1·4443	1·4685	—
20	1·1884	1·2191	0·9229	45	1·4558	—	—
21	1·1984	—	—	46	1·4673	1·4873	—
22	1·2083	1·2411	0·9164	47	1·4790	—	—
23	1·2184	—	—	48	1·4907	1·5065	—
24	1·2285	1·2629	0·9101	49	1·5025	—	—
25	1·2387	—	—	50	1·5143	1·5253	—

A, 6. DATA ON THE STRENGTH OF AQUEOUS SOLUTIONS OF THE COMMON ACIDS AND AMMONIUM HYDROXIDE

Reagent	*Approximate*			*Vol. required to make 1 litre of approx.* **N** *solution. Ml.*
	Per Cent by Weight	*Specific Gravity*	*Normality*	
Hydrochloric acid	35	1·18	11·3	89
Nitric acid	70–71	1·42	16·0	63
Sulphuric acid	96	1·84	36·0	28
Perchloric acid	70	1·66	11·6	86
Hydrofluoric acid	46	1·15	26·5	38
Phosphoric acid	85	1·69	14·7–44	23–68
Acetic acid	99·5	1·05	17·4	58
Ammonium hydroxide	$27(NH_3)$	0·90	14·3	71

A, 7. SAMPLES AND SOLUTIONS FOR ELEMENTARY ANALYSIS

There are two main methods which may be used for the supply of samples for analysis by elementary students, *i.e.*, for students who are just beginning the study of quantitative analysis. These are :—

1. **The use of pure (e.g., A.R.) substances of known composition.** This method has been largely adopted in the present treatise, and in the author's experience has given excellent results. It has been urged that the use of known amounts of material does not give the student practice in discovering for himself the quantity of precipitant to be used and solving similar simple problems which arise in analysis. This is true, but the writer feels that in the early stages of training it is far more important that the student should first acquire the experimental technique of quantitative analysis. The analysis of comparatively simple " unknown " solutions and solids is better reserved for a later stage when they will present comparatively little difficulty. However, many teachers prefer that quantitative exercises should be performed with solids or solutions of " unknown " composition. These are discussed below.

2. **The use of standard solutions prepared from A.R. solids.** A series of solutions, each containing one element or radical to be determined, is prepared of such concentration that, say, 20 to 30 ml. will provide a convenient quantity for analysis. For small classes the portion for analysis is measured out with a graduated pipette ; for large classes it is convenient to store the stock solution in a bottle with a burette permanently attached (Fig. 2–25 ; the burette may also be of the automatic-filling type as in Fig. 2–27). For each solution the instructor should draw a large scale graph in which the volume of solution is plotted against the quantity of the component present : this graph will provide a rapid means for checking the accuracy of the students' results.

Details of a few typical solutions are given below ; others may be similarly prepared (for list of A.R. reagents, see Section **A, 9**).

Aluminium : 70 g. of A.R. ammonium aluminium sulphate $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ per litre.

Ammonium : (i) 15 g. of A.R. ferrous ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$ per litre.
(ii) 4 g. of A.R. ammonium chloride NH_4Cl per litre.

Barium : 12 g. of A.R. barium chloride $BaCl_2,2H_2O$ per litre.

Bromide : 8 g. of A.R. potassium bromide KBr per litre.

Calcium : 20 g. of A.R. calcium carbonate $CaCO_3$ dissolved in a little dilute hydrochloric acid and diluted to 1 litre.

Carbonate : 30 g. of A.R. sodium carbonate Na_2CO_3 per litre.

Chloride : 8 g. of A.R. potassium chloride KCl per litre.

Chromium : 20 g. of A.R. potassium dichromate $K_2Cr_2O_7$ per litre.

Cobalt : 8 g. of A.R. cobalt ammonium sulphate $CoSO_4,(NH_4)_2SO_4,6H_2O$ per litre.

Copper : 30 g. of A.R. copper sulphate $CuSO_4,5H_2O$ per litre.

Iodide : 7 g. of A.R. potassium iodide KI per litre.

Iron : (i) 50 g. of A.R. ferric ammonium sulphate. $Fe_2(SO_4)_3, (NH_4)_2SO_4,24H_2O$ per litre.
(ii) 40 g. of A.R. ferrous ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$ per litre.

Lead : 12 g. of A.R. lead nitrate $Pb(NO_3)_2$ per litre (a little nitric acid should be present).

Magnesium : 25 g. of A.R. magnesium sulphate $MgSO_4,7H_2O$ per litre.

Manganese : 10 g. of A.R. potassium permanganate $KMnO_4$ per litre.

Mercury : 10 g. of A.R. mercuric chloride $HgCl_2$ per litre.

Nickel : 7 g. of A.R. nickel ammonium sulphate $NiSO_4,(NH_4)_2SO_4,6H_2O$ per litre.

Phosphate : 1·2 g. of A.R. microcosmic salt $Na(NH_4)HPO_4,4H_2O$ per litre (for the molybdate method).

Potassium : 7 g. of A.R. potassium chloride KCl per litre.

Silver : 14 g. of A.R. silver nitrate $AgNO_3$ per litre.

Sulphate : 7 g. of A.R. potassium sulphate K_2SO_4 per litre.

Zinc: (i) 30 g. of A.R. zinc sulphate $ZnSO_4,7H_2O$ per litre.
(ii) 40 g. of pure zinc ammonium sulphate $ZnSO_4,(NH_4)_2SO_4,6H_2O$ (see Section **IV, 34A**) per litre.

A, 8. ANALYSED SAMPLES

*ANALYSED SAMPLES FOR STUDENTS IN METALLURGICAL ANALYSIS**

These are comparatively inexpensive analysed samples and are particularly useful for the training of students in quantitative analysis ; a sheet giving the proportions of the various components determined is supplied. The use of many of these (" Ridsdale's Samples ") is suggested in the present volume.

Sample No.	*Name.*	*Constituents determined*
0	Mild carbon steel	Cd. C, P .
1	Mild carbon steel	Cd.C, Si, S, P, Mn .
2	Medium carbon steel	Cd.C, Si, S, P. Mn .
3, 21	High carbon steel	Cd. C, Si, S, P, Mn .
22	Nickel steel	Ni
3c	Alloy steel	Cd. C, Si, S, P, Mn, Cr, V, W .
4	Cast iron	Cd. C, Si, S, P, Mn, Gr. C .
12b	Foundry iron	Cd. C, Si, S, P, Mn .
13b	Hematite iron	Cd.C, Si, S, P, Mn, Gr. C .
5b	Brass	Cu, Zn, Sn, Pb .
7	Phosphor bronze	Cu, Zn, Sn, P, Pb .
19	Cupro-nickel	Cu, Ni, Mn .
23	Copper (tough)	As
10	Manganese bronze	Cu, Zn, Sn, Fe .
10c	Manganese bronze	Cu, Zn, Sn, Fe, Al, Mn, Pb .

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* Supplied by the Bureau of Analysed Samples, 3 Wilson Street, Middlesbrough, England. These were formerly called Ridsdale's Analysed Samples for Students, and are referred to by this name throughout the text.

Sample No.	*Name*	*Constituents determined*
Non-ferrous alloys		
86	Al-base casting alloy	Complete analysis.
53a	Bearing metal, Pb-base	do.
54a	Bearing metal, Sn-base	do.
63	Bearing metal, phosphor bronze	do.
37b	Brass, sheet	do.
52	Bronze, cast	do.
124	Ounce metal	do.
62	Bronze, manganese	do.
94	Zn-base, die casting alloy	do.
95	Do.	do.
96	Do.	do.
Ores		
69	Bauxite	Complete analysis.
26	Iron ore, Crescent	Al_2O_3, CaO, MgO .
29	Iron ore, Magnetite	Complete analysis.
28	Iron ore, Norrie	Mn (low).
27b	Iron ore, Sibley	SiO_2, P, Fe .
25b	Manganese ore	Mn, available oxygen.
56a	Phosphate rock (Tennessee)	P_2O_5,Fe_2O_3,Al_2O_3, etc.
120	Phosphate rock (Florida)	P_2O_5, Fe_2O_3, Al_2O_3, etc.
2a	Zinc ore	Zn
113	Zinc ore (Tri-State Concentrate)	Zn
Ceramic materials		
104	Burned magnesite	Complete analysis
76	Burned refractory (40% Al_2O_3)	do.
77	Burned refractory (60% Al_2O_3)	do.
78	Burned refractory (70% Al_2O_3)	do.
103	Chrome refractory	Cr_2O_3, SiO_2,Al_2O_3,FeO,CaO,MgO
97	Clay, flint	Complete analysis.
98	Clay, plastic	do.
70	Feldspar (potash)	do.
99	Feldspar (soda)	do.
79	Fluorspar	do.
1a	Limestone, argillaceous	do.
88	Limestone, dolomitic	do.
92	Glass, low boron	B_2O_3.
93	Glass, high boron	Complete analysis.
89	Glass, lead-barium	do.
91	Glass, opal	do.
80	Glass, soda-lime	do.
81	Glass sand	Fe_2O_3,Al_2O_3,TiO_2,ZrO_2,CaO,MgO .
102	Silica brick	Complete analysis.
112	Silicon carbide	do.

Sample No.	*Name*	*Constituents determined*
	Fineness standards	
46r	Cement (normal)	
47f	Cement (extra fine)	
114c	Cement (turbidimetric standard)	
	Melting-point standards	
44c	Aluminium	660·15°C.
45a	Copper	1,083°C.
49a	Lead	327·35°C.
42c	Tin	231·87°C.
43d	Zinc	419·52°C.
	Chemicals	
84	Acid potassium phthalate (99·97%)	Acidimetric value.
39e	Benzoic acid (99·99%)	Acidimetric and calorimetric value.
40c	Sodium oxalate	Oxidimetric value.
83	Arsenic trioxide (99·97%)	Oxidimetric value.
38b	Naphthalene	Calorimetric value.
17	Sucrose (cane sugar)	Calorimetric and saccharimetric value.
41	Dextrose (glucose)	Reducing value.
	Thermo-electric standards	
118	Alumel wire, no. 8 gage	E.m.f.. N.B.S. Pt no. 27, 0° to 1300°C.
119	Chromel wire, no. 8 gage	E.m.f. N.B.S. Pt no. 27, 0° to 1300°C.

A, 9. ANALYTICAL REAGENTS

In the following tables a list of the various analytical reagents at present available from British and American sources is given. The products of the following firms are listed :—

1 = Hopkin and Williams Ltd., 16 St. Cross St., London, E.C.2, England
2 = Mallinckrodt Chemical Works, 72–74 Gold Street, New York, N.Y., U.S.A.
3 = Baker and Adamson, Division of the General Chemical Co., 40 Rector Street, New York, N.Y., U.S.A.
4 = J. T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.
5 = The Coleman and Bell Co., Norwood, Ohio, U.S.A.*
6 = Merck and Co., Rahway, N.J., U.S.A.

*This firm terms most of its products of analytical reagent quality "Chemically pure" (C.P.) ; they have been incorporated in the tables.

In view of the limited number of analytical reagents at present available of purely British origin, Messrs. Hopkin and Williams Ltd., of St. Cross Street, London, E.C.2, England, have, at the author's request, made arrangements to supply any of the American products at short notice.

INORGANIC COMPOUNDS†

	Aluminium		
Metal Al	3	Fluoride AlF_3,xH_2O	3, 4
Acetate, basic	3, 4*, 6	Nitrate $Al(NO_3)_3, 9H_2O$	2, 3, 4, 5, 6
Ammonium sulphate $Al(SO_4)_3,(NH_4)_2SO_4,24H_2O$	1, 2, 3, 4, 5, 6	Oxide, ignited Al_2O_3	1, 3, 4, 6
Chloride $AlCl_3 6H_2O$	2, 3, 4, 5, 6	Potassium sulphate $Al_2(SO_4)_3,K_2SO_4,24H_2O$	1, 2, 3, 4, 5, 6
Chloride, anhydrous $AlCl_3$	2, 3, 4, 6	Sodium sulphate $Al_2(SO_4)_3,Na_2SO_4,24H_2O$	3, 4, 5
		Sulphate $Al_2(SO_4)_3,18H_2O$	1, 2, 3, 4, 5, 6
	Ammonium		
Hydroxide s.g. 0·88-0·90	1, 2, 3, 4, 5, 6	Metavanadate NH_4VO_3	1, 5
Acetate $NH_4C_2H_3O_2$	1, 2, 3, 4, 5, 6	Molybdate $(NH_4)_6Mo_7O_{24},4H_2O$	1, 2, 3, 4, 5, 6
Arsenate	4	Nitrate NH_4NO_3	1, 2, 3, 4, 5, 6
Bicarbonate NH_4HCO_3	1, 3, 4, 5	Oxalate $(NH_4)_2C_2O_4,H_2O$	1, 2, 3, 4, 5, 6
Bichromate $(NH_4)_2Cr_2O_7$	2, 3, 6	Perchlorate NH_4ClO_4	4, 5
Bisulphate NH_4HSO_4	2, 3, 4, 5, 6	Persulphate $(NH_4)_2S_2O_8$	1, 2, 3, 4, 5, 6
Bitartrate $NH_4.HC_4H_4O_6$	4, 5	Phosphate, primary, $NH_4H_2PO_4$	2, 3, 4, 5, 6
Borate	4	Phosphate, secondary, $(NH_4)_2HPO_4$	1, 2, 3, 4, 5, 6
Bromide NH_4Br	2, 3, 4, 5, 6	Sulphate $(NH_4)_2SO_4$	1, 2, 3, 4, 5, 6
" Carbonate "	1, 2, 3, 4, 5, 6	Sulphide solution, light $(NH_4)_2S$ + Aq.	2, 3, 4, 5
Chloride NH_4Cl	1, 2, 3, 4, 5, 6	Sulphide solution, yellow $(NH_4)_2S_x$ + Aq.	1, 2, 3, 4, 5, 6
Chromate $(NH_4)_2CrO_4$	2, 3, 4, 5, 6	Tartrate $(NH_4)_2.C_4H_4O_6$	3, 4, 5, 6
Chromium sulphate $(NH_4)_2SO_4,Cr_2(SO_4)_3,24H_2O$	3	Thiocyanate NH_4CNS	1, 2, 3, 4, 5, 6
Citrate $(NH_4)_2H.C_6H_5O_7$	2, 3, 4, 5, 6		
Fluoride NH_4F	1, 3, 4		
Formate $HCOONH_4$	3, 4, 6		
Iodide NH_4I	2, 3, 4, 5		
	Antimony		
Metal Sb	2, 3, 4	Sulphate $Sb_2(SO_4)_3$	5
Pentoxide Sb_2O_5	5	Tribromide $SbBr_3$	5
Pentachloride $SbCl_5$	3, 4, 5	Trichloride $SbCl_3$	1, 2, 3, 4, 5, 6
otassium tartrate $2K(SbO)C_4H_4O_6,H_2O$	1*, 3, 4, 5	Trioxide Sb_2O_3	3, 4, 5

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† All organic compounds containing inorganic cations will be included under inorganic compounds.

* Throughout these tables an asterisk indicates that the anhydrous compound is also available.

	Arsenic		
Arsenic As	5	Trichloride $AsCl_3$	3
Arsenic acid H_3AsO_4	2, 3, 6	Trioxide As_2O_3	1, 2, 3, 4, 5, 6
Pentoxide As_2O_5	2, 3, 4, 5		
	Barium		
Acetate $Ba(C_2H_3O_2)_2,H_2O$	1, 2, 3, 4, 5, 6	Nitrate $Ba(NO_3)_2$	1, 2, 3, 4, 5, 6
Bromate $Ba(BrO_3)_2,H_2O$	2	Oxalate BaC_2O_4,H_2O	4, 5
Bromide $BaBr_2, 2H_2O$	2, 5	Oxide BaO	3
Carbonate $BaCO_3$	1, 2, 3, 4, 5, 6	Phosphate $Ba_3(PO_4)_2$	4, 5
Chlorate $Ba(ClO_3)_2,H_2O$	3, 4, 5, 6	Sulphate $BaSO_4$	2, 3, 4, 5, 6
Chloride $BaCl_2, 2H_2O$	1, 2, 3, 4, 5, 6	Sulphite $BaSO_3$	4
Chromate $BaCrO_4$	4, 5	Tartrate $Ba.C_4H_4O_6$	5
Dioxide, anhydrous BaO_2	2, 3, 4, 5, 6	Thiocyanate $Ba(CNS)_2,3H_2O$	3
Dioxide $BaO_2,8H_2O$	4	Thiosulphate BaS_2O_3,H_2O	4
Fluoride BaF_2	3		
Hydroxide $Ba(OH)_2,8H_2O$	1, 2, 3, 4, 5, 6		
	Bismuth		
Metal Bi	2, 3, 4, 5, 6	Sub-nitrate $BiONO_3,H_2O$	2, 3, 4, 5
Nitrate $Bi(NO_3)_3,5H_2O$	2, 3, 4, 5, 6	Trichloride $BiCl_3$	2, 3, 4, 5, 6
Oxychloride BiOCl	3, 4	Trioxide Bi_2O_3	3, 4
Sub-carbonate Bi_2O_3,CO_2,H_2O	4, 5, 6		

Boric Acid H_3BO_3	1, 2, 3, 4, 5
Boric anhydride	6
Bromine Br_2	1, 2, 3, 4, 5

	Cadmium		
Acetate $Cd(C_2H_3O_2)_2,2H_2O$	2, 3, 4, 5, 6	Iodide CdI_2	1, 2, 3, 4, 5, 6
Bromide $CdBr_2,4H_2O$	3, 4, 5, 6	Nitrate $Cd(NO_3)_2,4H_2O$	2, 3, 4, 5, 6
Carbonate $CdCO_3$	2, 3, 4, 5, 6	Oxide CdO	3, 4, 5
Chloride $2CdCl_2,5H_2O$	2, 3, 4, 5*, 6	Potassium iodide $CdI_2,2KI,2H_2O$	2
Hydroxide $Cd(OH)_2$	3, 4, 5	Sulphate $3CdSO_4,8H_2O$	1, 2, 3, 4*, 5, 6
	Calcium		
Acetate $Ca(C_2H_3O_2)_2,H_2O$	2, 3, 4, 5, 6	Nitrate $Ca(NO_3)_2,4H_2O$	2, 3, 4, 5, 6
Arsenate	4	Oxalate CaC_2O_4,H_2O	3, 4, 5
Bromide $CaBr_2$	3, 4, 5	Oxide CaO	3, 6
Carbonate $CaCO_3$	1, 2, 3, 4, 5, 6	Phosphate, primary, $Ca(H_2PO_4)_2,H_2O$	2, 3, 4, 5, 6
Chloride $CaCl_2,6H_2O$	1, 2, 3, 4, 5, 6	Phosphate, secondary $CaHPO_4,2H_2O$	2, 3, 4, 5, 6
Chloride, anhydrous (96%) $CaCl_2$	2, 3, 4, 5, 6	Phosphate, tertiary $Ca_3(PO_4)_2$	2, 3, 4, 5, 6
Chromate $CaCrO_4,2H_2O$	4, 5	Sulphate $CaSO_4,2H_2O$	2, 3, 4, 5, 6
Citrate $Ca_3(C_6H_5O_7)_2,4H_2O$	3, 4, 5	Sulphide CaS	3
Fluoride CaF_2	3, 4, 5	Sulphite $CaSO_3,2H_2O$	3, 4, 5
Formate $Ca(HCO_2)_2$	4, 5, 6	Tartrate $CaC_4H_4O_6,4H_2O$	3, 4, 5
Hydroxide $Ca(OH)_2$	2, 3	Tungstate	5
Iodide CaI_2	4		

Cerium nitrate	3
Chloroplatinic acid $H_2PtCl_6,6H_2O$	2, 3

Chromium

Acetate $Cr(C_2H_3O_2)_2,xH_2O$	2, 3, 4, 5
Ammonium sulphate $Cr_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$	4
Bromide $CrBr_3,xH_2O$	3, 5
Carbonate, basic	5
Chloride $CrCl_3,6H_2O$	2, 3, 4, 5
Hydroxide Cr_2O_3,xH_2O	4
Nitrate $Cr(NO_3)_3,9H_2O$	2, 3, 4, 5
Potassium sulphate $Cr_2(SO_4)_3,K_2SO_4,24H_2O$	1, 2, 3, 4, 5, 6
Sesquioxide Cr_2O_3	3, 4, 5
Sulphate $Cr_2(SO_4)_3,xH_2O$	2, 3, 4, 5, 6
Trioxide CrO_3	1, 2, 3, 4, 5, 6

Cobalt

Metal (98-99%)	3, 4, 5
Acetate $CO(C_2H_3O_2)_2,4H_2O$	2, 3, 4, 5, 6
Ammonium sulphate $CoSO_4,(NH_4)_2SO_4,6H_2O$	4, 5
Carbonate $CoCO_3$	3, 4, 5, 6
Chloride $CoCl_2,6H_2O$	1, 2, 3, 4, 5, 6
Chromate $CoCrO_4$	5
Nitrate $Co(NO_3)_2,6H_2O$	1, 2, 3, 4, 5, 6
Oxalate $CoC_2O_4,2H_2O$	4, 5
Oxide, black Co_2O_3	3, 4
Sulphate $CoSO_4,7H_2O$	1, 2, 3, 4, 5, 6

Copper

Metal Cu	1, 2, 6
Acetate $Cu(C_2H_3O_2)_2,H_2O$	1, 2, 3, 4, 5, 6
Aceto-arsenite $(CuO.As_2O_3)_3(C_2H_3O_2)_2Cu$	4
Ammonium chloride $CuCl_2,2NH_4Cl,2H_2O$	1, 2, 3, 4, 5, 6
Ammonium sulphate $CuSO_4,(NH_4)_2SO_4,6H_2O$	3, 4, 5
Borate (ic)	5
Bromide (ic) $CuBr_2$	2, 3, 4, 5, 6
Bromide (ous) Cu_2Br_2	3, 4, 5
Carbonate, basic *ca.* $CuCO_3,Cu(OH)_2$	2, 3, 4, 5, 6
Chloride (ic) $CuCl_2,2H_2O$	1, 2, 3, 4*, 5, 6
Chloride (ous) Cu_2Cl_2	1, 2, 3, 4, 5, 6
Cyanide (ous) $Cu_2(CN)_2$	3, 4
Ferrocyanide $Cu_2Fe(CN)_6$	5
Nitrate $Cu(NO_3)_2,3H_2O$	1, 2, 3, 4, 5, 6
Oxalate $2CuC_2O_4,H_2O$	4, 5
Oxide (ic) CuO	1, 2, 3, 4, 5, 6
Oxide (ous) Cu_2O	3, 4, 5
Phosphate $Cu_3(PO_4)_2,2H_2O$	4
Potassium chloride $CuCl_2,2KCl,2H_2O$	3, 4, 6
Potassium sulphate $CuSO_4,K_2SO_4,6H_2O$	3, 4
Sulphate $CuSO_4,5H_2O$	1, 2, 3, 4, 5, 6
Sulphate, anhydrous $CuSO_4$	2, 3, 4, 5, 6
Sulphide (ic) CuS	2, 3, 4, 5
Sulphide (ous) Cu_2S	2, 5
Tartrate $CuC_4H_4O_6,3H_2O$	4

Devarda's metal	6
Eshka's mixture 2MgO : $1Na_2CO_3$	1, 2, 3, 4, 5, 6

Iron

Ferric compounds

Ammonium oxalate $Fe(NH_4)_3(C_2O_4)_3,3H_2O$	4, 6
Ammonium sulphate $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$	1, 2, 3, 4, 5, 6
Chloride $FeCl_3,6H_2O$	1, 2, 3, 4, 5, 6
Chloride, anhydrous $FeCl_3$	1, 3, 5
Nitrate $Fe(NO_3)_3,9H_2O$	2, 3, 4, 5, 6
Oxide Fe_2O_3	3, 4
Phosphate $FePO_4,4H_2O$	3, 4, 5
Sulphate $Fe_2(SO_4)_3,xH_2O$	2, 3, 4, 5, 6

Ferrous compounds

Ammonium chloride $FeCl_2,2NH_4Cl,H_2O$	4, 5
Ammonium sulphate $FeSO_4,(NH_4)_2SO_4,6H_2O$	1, 2, 3, 4, 5, 6
Chloride $FeCl_2$ $4H_2O$	2, 3, 4, 5, 6
Oxalate $FeC_2O_4,2H_2O$	5
Phosphate	3, 5
Sulphate $FeSO_4,7H_2O$	1, 2, 3, 4, 5, 6

Fusion mixture	1
Gold Chloride $HAuCl_4,3H_2O$	2, 3, 6
Hydrazine sulphate N_2H_4,H_2SO_4	1, 5, 6
Hydrogen peroxide, 3% H_2O_2	1, 2, 3, 4
Hydrogen peroxide, 6% H_2O_2	1
Hydrogen peroxide, 30% H_2O_2	4
Hydrobromic acid 46–48% HBr	1, 2, 3, 4, 5, 6
Hydrochloric acid 35–37% HCl	1, 2, 3, 4, 5, 6
Hydrofluoric acid 40–48% HF	1, 2, 3, 4, 5, 6
Hydriodic acid 47% HI	2, 5
Hydriodic acid 54–56% and 64–68% HI	1, 6
Hydrofluosilicic acid 27–30% H_2SiF_6	3, 4, 5, 6
Hydroxylamine hydrochloride NH_2OH,HCl	1, 3, 4, 5, 6
Hydroxylamine sulphate $(NH_2OH)_2,H_2SO_4$	3, 5
Iron wire 99·9% Fe	2, 3, 6
Iodine I_2	1, 2, 3, 4, 5, 6
Iodic acid HIO_3	1, 2, 3, 4, 5, 6
Iodine pentoxide I_2O_5	2, 6

Lead

Metal Pb	1, 2, 6	Chromate $PbCrO_4$	2, 3, 4, 5, 6
Acetate $Pb(C_2H_3O_2),3H_2O$	1, 2, 3, 4, 5, 6	Dioxide PbO_2	1, 2, 3, 4, 5, 6
Acetate, basic *ca.* $5Pb(C_2H_3O_2)_2,2PbO$	1, 2, 3, 5, 6	Nitrate $Pb(NO_3)_2$	1, 2, 3, 4, 5
Arsenate $PbHAsO_4$	4	Oxide, yellow, PbO	1, 2, 3, 4, 5, 6
Borate $Pb(BO_2)_2,H_2O$	4	Oxide, red, Pb_3O_4	2, 3, 4, 5, 6
Carbonate, basic *ca.* $2PbCO_3,Pb(OH)_2$	2, 3, 4, 5, 6	Oxalate PbC_2O_4	4
Chloride $PbCl_2$	2, 3, 4, 5, 6	Phosphate $Pb_3(PO_4)_2$	2, 4, 5
		Sulphate $PbSO_4$	2, 3, 4, 5, 6
		Tartrate $PbC_4H_4O_6$	4

Lithium

Acetate	5	Fluoride LiF	3, 4
Bromide LiBr	5	Nitrate $LiNO_3$	2, 3, 4, 5, 6
Carbonate Li_2CO_3	2, 3, 4, 5	Oxalate	5
Chloride LiCl	2, 3, 4, 5, 6	Sulphate Li_2SO_4,H_2O	2, 3, 4, 5, 6

Magnesium

Metal, turnings Mg	2	Citrate	4
Acetate $Mg(C_2H_3O_2)_2,4H_2O$	2, 3, 4, 5, 6	Fluoride MgF_2	4
Ammonium chloride $MgCl_2,NH_4Cl,6H_2O$	1, 2, 3, 4, 5	Nitrate $Mg(NO_3)_2,6H_2O$	2, 3, 4, 5, 6
Bromide $MgBr_2,6H_2O$	3, 4, 5, 6	Oxide MgO	1, 2, 3, 4, 5, 6
Carbonate, basic *ca.* $3MgCO_3,Mg(OH)_2,3H_2O$	2, 3, 4, 5, 6	Oxalate $MgC_2O_4,2H_2O$	4
Chloride $MgCl_2,6H_2O$	1, 2, 3, 4, 5, 6	Perchlorate $Mg(ClO_4)_2$	5
Chromate	4	Phosphate, secondary $MgHPO_4,3H_2O$	4
		Phosphate, tertiary $Mg_3(PO_4)_2,8H_2O$	2, 4
		Sulphate $MgSO_4,7H_2O$	1,2*,3,4,5*,6

Manganese

Acetate $Mn(C_2H_3O_2),4H_2O$	4, 5	Dioxide MnO_2	3, 5, 6
Borate	4	Nitrate $Mn(NO_3)_2$ 50% solution	2, 3, 4, 5, 6
Bromide	5	Phosphate	4
Carbonate $MnCO_3$	3, 4, 5, 6	Sulphate $MnSO_4,4H_2O$	1, 2, 3, 4, 5, 6
Chloride $MnCl_2,4H_2O$	1, 2, 3, 4, 5, 6		

Mercury

Metal Hg	1, 2, 3, 4, 5, 6		
Mercuric compounds		*Mercurous compounds*	
Acetate $Hg(C_2H_3O_2)_2$	2, 3, 4, 5, 6	Chloride Hg_2Cl_2	1, 2, 3, 4, 5, 6
Bromide $HgBr_2$	2, 3, 4, 5, 6	Iodide Hg_2I_2	5
Chloride $HgCl_2$	1, 2, 3, 4, 5, 6	Nitrate $Hg_2(NO_3)_2,2H_2O$	1, 2, 3, 4, 5, 6
Cyanide $Hg(CN)_2$	2, 4, 6	Sulphate Hg_2SO_4	2, 3, 4, 5
Iodide HgI_2	2, 3, 4, 5, 6		
Nitrate $Hg(NO_3)_2,xH_2O$	2, 3, 4, 5, 6		
Oxide, red HgO	1, 2, 3, 4, 5, 6		
Oxide, yellow HgO	2, 3, 4, 5, 6		
Sulphate $HgSO_4$	2, 3, 4, 5, 6		
Sulphide HgS	4		

Molybdenum trioxide MoO_3	1, 2, 3, 4, 5, 6
Molybdic acid (85% MoO_3)	1, 2, 3, 4, 5, 6

Nickel

Metal Ni	2, 4	Chloride $NiCl_2,6H_2O$	1, 2, 3, 4, 5, 6
Acetate $Ni(C_2H_3O_2)_2,4H_2O$	3, 4, 5, 6	Nitrate $Ni(NO_3)_2,6H_2O$	2, 3, 4, 5, 6
Ammonium sulphate $NiSO_4,(NH_4)_2SO_4,6H_2O$	2, 3, 4, 5, 6	Oxalate $NiC_2O_4,2H_2O$	4, 5
Bromide	5	Oxide, grey-black (ic)	4, 5
Carbonate, basic *ca.* $2NiCO_3,3Ni(OH)_2,4H_2O$	3, 4, 5, 6	Oxide, green (ous) NiO	4
		Phosphate $Ni_3(PO_4)_2,7H_2O$	4, 5
		Sulphate $NiSO_4,6H_2O$	1, 2, 3, 4, 5, 6
		Tartrate	4

Nitric acid, sp. gr. 1·42, 69–72% HNO_3	1, 2, 3, 4, 5, 6
Nitric acid, sp. gr. 1·5, fuming 89–95% HNO_3	1, 3, 4, 5, 6
Oxalic acid, cryst., $H_2C_2O_4,2H_2O$	1, 2, 3, 4, 5, 6
Oxalic acid, anhydrous $H_2C_2O_4$	3, 4, 5
Palladium chloride	5
Perchloric acid, 20% or 60% $HClO_4$	1, 2, 3, 4, 5, 6
Perchloric acid, 70–72% $HClO_4$	2, 3, 4, 5, 6
Phosphoric anhydride P_2O_5	2, 3, 4, 5, 6
Phosphoric acid, ortho, 85% H_3PO_4	1, 2, 3, 4, 5, 6
Phosphoric acid, meta, sticks	2, 3, 5, 6
Phosphorous acid, cryst. H_3PO_3	3
Phosphorus oxychloride $POCl_3$	2, 3, 5, 6
Phosphorus pentachloride PCl_5	2, 3, 5, 6
Phosphorus trichloride PCl_3	2, 3, 4, 5, 6
Phosphomolybdic acid $P_2O_5,20MoO_3,xH_2O$	1, 2, 3, 4, 5, 6
Phosphotungstic acid $P_2O_5,24MoO_3,xH_2O$	1, 2, 3, 4, 5, 6

Potassium

Acetate $KC_2H_3O_2$	2, 3, 4, 5, 6	Bichromate $K_2Cr_2O_7$	1, 2, 3, 4, 5, 6
Ammonium sulphate $K_2SO_4,(NH_4)_2SO_4$	4, 5	Binoxalate KHC_2O_4	3, 4, 6
Arsenate, primary KH_2AsO_4	3, 4, 5, 6	Bisulphate $KHSO_4$	1, 2, 3, 4, 5, 6
Arsenite $KAsO_2$	3, 4, 5, 6	Bitartrate $KHC_4H_4O_6$	1, 2, 3, 4, 5, 6
Bicarbonate	1, 2, 3, 4, 5, 6	Bromate $KBrO_3$	1, 2, 3, 4, 5, 6
		Bromide	1, 2, 3, 4, 5, 6

Potassium—*continued*

Carbonate, anhydrous K_2CO_3	1, 2, 3, 4, 5, 6	Nitrite KNO_2	2, 3, 4, 5
Carbonate, cryst., $2K_2CO_3,3H_2O$	4, 5	Oxalate $K_2C_2O_4,H_2O$	1, 2, 3, 4, 5, 6
Chlorate $KClO_3$	1, 2, 3, 4, 5, 6	Perchlorate $KClO_4$	3, 4, 5, 6
Chloride KCl	1, 2, 3, 4, 5	Periodate KIO_4	3, 4
Chloroplatinate K_2PtCl_6	5	Permanganate $KMnO_4$	1, 2, 3, 4, 5, 6
Chromate K_2CrO_4	1, 2, 3, 4, 5, 6	Persulphate $K_2S_2O_8$	1, 2, 3, 4, 5, 6
Citrate $K_3C_6H_5O_7,H_2O$	1, 2, 3, 4, 5, 6	Phosphate, primary KH_2PO_4	1, 2, 3, 4, 5, 6
Cyanate KCNO	3, 4, 5	Phosphate, secondary K_2HPO_4	2, 3, 4, 5, 6
Cyanide KCN	1, 2, 3, 4, 5, 6	Phosphate, tertiary K_3PO_4	2, 3, 4, 5, 6
Ferricyanide $K_3Fe(CN)_6$	1, 2, 3, 4, 5, 6	Pyroantimonate	4, 5
Ferrocyanide $K_4Fe(CN)_6,3H_2O$	1, 2, 3, 4, 5, 6	Pyrophosphate $K_4P_2O_7,3H_2O$	4, 5
Fluoride KF	2, 3, 4, 5, 6	Sodium tartrate $KNaC_4H_4O_6,4H_2O$	1, 2, 3, 4, 5, 6
Formate HCOOK	4, 5	Sulphate K_2SO_4	1, 2, 3, 4, 5, 6
Hydrogen phthalate $KHC_8H_4O_4$	1, 2, 3, 4, 5, 6	Sulphite K_2SO_3	3, 4, 5
Hydroxide KOH	1, 2, 3, 4, 5, 6	Tartrate $2K_2C_4H_4O_6,H_2O$	2, 3, 4, 5, 6
Iodate KIO_3	1, 2, 3, 4, 5, 6	Tetraborate $K_2B_4O_7,5H_2O$	3, 4
Iodide KI	1, 2, 3, 4, 5, 6	Tetroxalate $KHC_2O_4,H_2C_2O_4,2H_2O$	1, 4, 5, 6
Mercuric iodide	4	Thiocyanate KCNS	1, 2, 3, 4, 5, 6
Metabisulphite	1, 2, 3, 4, 5, 6		
Molybdate	5		
Nitrate KNO_3	1, 2, 3, 4, 5, 6		

Silicic acid, powder	2, 3, 4, 5, 6

Silver

Metal, powder Ag	2	Lactate $AgC_3H_5O_3,H_2O$	3
Bromide AgBr	5	Nitrate $AgNO_3$	1, 2, 3, 4, 5, 6
Carbonate Ag_2CO_3	2, 3	Oxide Ag_2O	3
Chloride AgCl	2, 3, 4, 5	Sulphate Ag_2SO_4	2, 3, 4, 5, 6
Iodate	6		

Sodium

Metal, Na	2, 3, 4, 5, 6	Bitartrate $NaHC_4H_4O_6,H_2O$	2, 3, 4, 5, 6
Acetate $NaC_2H_3O_2,3H_2O$	1, 2, 3, 4, 5, 6	Borate $NaB_4O_7,10H_2O$	1, 2, 3, 4, 5, 6
Acetate, anhydrous $NaC_2H_3O_2$	1, 2, 3, 4, 5, 6	Bromate $NaBrO_3$	2, 3, 4, 5, 6
Aluminate $Na_2Al_2O_4$	3	Bromide NaBr	2, 3, 4, 5, 6
Ammonium phosphate $NaNH_4HPO_4,4H_2O$	2, 3, 4, 5, 6	Carbonate $Na_2CO_3,10H_2O$	1, 2, 3, 6
Arsenate $Na_2HAsO_4,7H_2O$	2, 3, 4, 5, 6	Carbonate Na_2CO_3,H_2O	2, 4
Arsenite $NaAsO_2$	2, 3, 4, 5, 6	Carbonate, anhydrous Na_2CO_3	1, 2, 3, 4, 5, 6
Bicarbonate $NaHCO_3$	1, 2, 3, 4, 5, 6	Chlorate $NaClO_3$	3, 4, 5, 6
Bichromate $Na_2Cr_2O_7,2H_2O$	2, 3*, 4*, 5, 6	Chloride NaCl	1, 2, 3, 4, 5, 6
Binoxalate $NaHC_2O_4,H_2O$	4	Chromate $Na_2CrO_4,4H_2O$	2, 3, 4, 5, 6
Bisulphate, anhydrous $NaHSO_4$	1, 2, 3, 4, 5, 6	Citrate $2Na_3C_6H_5O_7,11H_2O$	1, 2, 3, 4, 5, 6
Bisulphate, cryst., $NaHSO_4,H_2O$	2, 3, 4, 5	Cobaltinitrite $Na_3Co(NO_2)_6$	1, 2, 3, 4, 5, 6
Bisulphite $NaHSO_3$	2, 4, 5, 6	Cyanide NaCN	2, 3, 4, 5, 6
		Fluoride NaF	2, 3, 4, 5, 6

Sodium—*continued*

Ferrocyanide $Na_4Fe(CN)_6,10H_2O$	4, 5	Phosphate, tertiary $Na_3PO_4,12H_2O$	2, 3, 4, 5, 6
Formate HCOONa	2, 3, 4, 5, 6	Pyrophosphate $Na_4P_2O_7,10H_2O$	2, 3, 4*, 5, 6
Hydroxide NaOH	1, 2, 3, 4, 5, 6	Salicylate $NaC_7H_5O_3$	2, 3, 4, 5, 6
Hypophosphite NaH_2PO_2,H_2O	4, 6	Silicate $Na_2SiO_3,9H_2O$	4
Iodate $NaIO_3$	2, 3, 4, 5, 6	Stannate $NaSnO_3,3H_2O$	4
Iodide NaI	2, 3, 4, 5, 6	Sulphate $Na_2SO_4,10H_2O$	1, 2, 3, 4, 5, 6
Metabisulphite NaS_2O_5	3	Sulphate, anhydrous Na_2SO_4	1, 2, 3, 4, 5, 6
Metaphosphate $NaPO_3$	3, 4	Sulphide $Na_2 S, 9H_2O$	1, 2, 3, 4, 5, 6
Molybdate $Na_2MoO_4,2H_2O$	2, 3, 4, 5, 6	Sulphite $Na_2SO_3,7H_2O$	3, 4, 5
Nitrate $NaNO_3$	1, 2, 3, 4, 5, 6	Sulphite, anhydrous Na_2SO_3	2, 3, 4, 5, 6
Nitrite $NaNO_2$	1, 2, 3, 4, 5, 6	Tartrate $Na_2C_4H_4O_6,2H_2O$	2, 3, 4, 5, 6
Nitroprusside $Na_2Fe(CN)_5NO,H_2O$	1, 2, 3, 4, 5, 6	Tetroxalate $NaHC_2O_4,Na_2C_2O_4,2H_2O$	4, 5
Oxalate $Na_2C_2O_4$	1, 2, 3, 4, 5, 6	Thiocyanate NaCNS	2, 3, 4, 5
Perborate $NaBO_3,4H_2O$	2, 3, 4	Thiosulphate $Na_2S_2O_3,5H_2O$	1, 2, 3, 4, 5, 6
Peroxide, 85% + Na_2O_2	1, 2, 3, 4, 5, 6	Thiosulphate anhydrous $Na_2S_2O_3$	2, 3, 4
Phosphate, primary NaH_2PO_4,H_2O	2, 3, 4, 5, 6	Tungstate $Na_2WO_4,2H_2O$	1, 2, 3, 4, 5, 6
Phosphate, secondary, cryst., $Na_2HPO_4,12H_2O$	1, 2, 3, 4, 5, 6		
Phosphate, secondary, anhydrous Na_2HPO_4	1, 2, 3, 4, 6		

Tin

Metal Sn	1, 2, 3, 4, 5, 6		
Stannous compounds		*Stannic compounds*	
Chloride $SnCl_2,2H_2O$	1, 2, 3, 4, 5, 6	Chloride $SnCl_4,5H_2O$	2, 3, 4, 5, 6
Oxide SnO	3, 4, 5	Chloride, anhydrous $SnCl_4$	3, 4
Sulphide SnS	3	Oxide SnO_2	3, 4, 5

Strontium

Acetate $2Sr(C_2H_3O_2)_2,H_2O$	2, 3, 4, 5, 6	Hydroxide $Sr(OH)_2,8H_2O$	4, 5
Bromide $SrBr_2,6H_2O$	4, 5	Nitrate $Sr(NO_3)_2$	2, 3, 4, 5, 6
Carbonate $SrCO_3$	2, 3, 4, 5, 6	Oxalate SrC_2O_4,H_2O	4, 5
Chloride $SrCl_2,6H_2O$	2, 3, 4, 5, 6	Phosphate	4
Fluoride SrF_2	3	Sulphate $SrSO_4$	3, 4, 5, 6

Silicotungstic acid $SiO_2,12WO_3,26H_2O$	3, 4, 6
Sulphuric acid, 95–98% H_2SO_4	1, 2, 3, 4, 5, 6
Sulphuric acid, fuming, 15% SO_3	3, 4, 5, 6
Thorium nitrate $Th(NO_3)_4,12H_2O$	3, 4, 5
Tungstic acid	5
Uranyl acetate $UO_2(C_2H_3O_2)_2,2H_2O$	1, 2, 3, 4, 5, 6
Uranyl nitrate $UO_2(NO_3)_2,6H_2O$	1, 2, 3, 4, 5, 6

Zinc

Metal Zn	1, 2, 3, 4, 5, 6	Nitrate $Zn(NO_3)_2,6H_2O$	2, 3, 4, 5, 6
Acetate $Zn(C_2H_3O_2)_2,2H_2O$	2, 3, 4, 5, 6	Oxalate $ZnC_2O_4,2H_2O$	4
Bromide $ZnBr_2$	4, 5	Oxide ZnO	1, 2, 3, 4, 5, 6
Carbonate, basic	2, 3, 4, 5, 6	Sulphate $ZnSO_4,7H_2O$	1, 2, 3, 4, 5, 6
Chromate	4	Sulphate, dry $ZnSO_4,H_2O$	3, 4
Chloride, anhydrous $ZnCl_2$	2, 3, 4, 5, 6	Sulphide, ZnS	5

ORGANIC COMPOUNDS

Acetamide	3, 5, 6	Amyl acetate	1, 2
Acetic anhydride	1, 2, 3, 4, 5, 6	Amyl alcohol, primary, normal	2
Acetic acid, glacial	1, 2, 3, 4, 5, 6	*iso*-Amyl alcohol	2, 3, 4, 5
Acetone	1, 2, 3, 4, 5, 6	*iso*-Amyl nitrite	1, 5
Acetonitrile	6	Aniline	1, 2, 3, 4, 5, 6
Acetyl bromide	1	Aniline hydrochloride	3, 4, 5
Acetyl chloride	1, 3, 5, 6	Aniline nitrate	5
dl-Alanine	5	Aniline sulphate	3, 4, 5
Allyl alcohol	5	*l*-Arabinose	5
Aminoacetic acid	1, 5		

Benzaldehyde	5	Benzyl alcohol	5
Benzene	1, 5, 6	Benzyl benzoate	5
Benzidine	6	Benzyl chloride	2, 3, 4, 5
Benzidine acetate	5	Bromobenzene	6
Benzidine hydrochloride	5	Bromo-cresol purple	6
Benzidine sulphate	5	*iso*-Butyl acetate	5
Benzil	5	*n*-Butyl acetate	5
Benzoic acid	1, 2, 3, 4, 5, 6	*iso*-Butyl alcohol	5
Benzophenone	5	*n*-Butyl alcohol	2, 3, 4, 5
Benzoyl chloride	1, 2, 3, 4, 5	*n*-Butyric acid	2

Carbon disulphide	1, 2, 3, 4, 5, 6	Cinnamic acid	5
Carbon tetrachloride	1, 2, 3, 4, 5, 6	Citric acid	1, 2, 3, 4, 5, 6
Carminic acid	6	Congo red	6
Chloroform	1, 2, 3, 4, 5, 6	Cupferron	5

Dextrose	6	Dimethyl yellow	1
Dimethylaminobenzene	1	Diphenylamine	1, 5, 6
p-Dimethylamino-benzaldehyde	1, 5	Diphenylamine hydrochloride	5
Dimethylaniline	1, 5	Dulcitol	
Dimethylglyoxime	1, 2, 3, 5, 6		

Ether, anhydrous	1, 2, 3, 4, 5, 6	Ethyl benzoate	5
Ethyl acetate	2, 3, 4, 5	Ethyl bromide	2, 3, 5, 6
Ethyl acetoacetate	5, 6	Ethylene bromide	5, 6
Ethyl alcohol, 90%, 98–100%	1	Ethyl chlorcarbonate	6
		Ethyl iodide	2, 3

Formaldehyde solution, *ca.* 37% by weight	1, 2, 3, 4, 5, 6
Formic acid, sp. gr., 1·20, 87–90%	1, 2, 3, 4, 5, 6

Gallic acid	5, 6	Guanidine carbonate	1
Glycerine	1, 2, 3, 4, 5, 6		

ORGANIC COMPOUNDS—*continued*

Hippuric acid	5	*p*-Hydroxyphenylarsonic acid	2
Isatin	5		
Lactose	1, 2, 3, 4, 5	Lactic acid, 85–88%	1, 2, 3, 4, 5, 6
Maltose	5	Methyl alcohol	1, 2, 3, 4, 5
d-Mannitol (mannite)	5	Methyl benzoate	5
d-Mannose	5	Methyl ethyl ketone	6
Meta nitraniline	5	Methylene blue	6
Meta phenylene diamine hydrochloride	5	Methyl iodide	2, 3
Meta toluylene diamine hydrochloride	5	Methyl orange	1, 6
		Methyl red	1
		Monochloroacetic acid	1, 2, 3, 4, 5, 6
Naphthalene	3, 4	Nitrobenzene	1
α-Naphthol	1	*p*-Nitrobenzoyl chloride	6
β-Naphthol	1	*p*-Nitrochlorbenzene	6
α-Naphthylamine	1	Nitroso-β-naphthol	6
α-Naphthylamine hydrochloride	4		
Oxalic acid, cryst.	1, 2, 3, 4, 5, 6	Oxine	6
Oxalic acid, anhydrous	3, 4, 5		
Petroleum ether (various b.p. ranges)	1, 2, 3, 4, 5	Phthalic anhydride	2, 3, 4, 5, 6
Phenol	1, 2, 3, 4, 5, 6	Picramic acid	5
Phenol red	6	Picric acid	1, 2, 3, 4, 5, 6
Phenolphthalein	1, 2, 3, 4	*n*-Propyl alcohol	5
Phenylhydrazine hydrochloride	1, 3, 4, 5	*iso*-Propyl alcohol	5
Phloroglucinol	1, 3, 5, 6	Pyridine	1, 2, 3, 4, 5, 6
		Pyrocatechol	3
		Pyrogallic acid	2, 3, 4, 5, 6
Quinhydrone	1, 3, 5, 6	Quinoline	5
Raffinose hydrate	5	Rosolic acid	6
Resorcinol	1, 2, 3, 5, 6		
Saccharin	4	Sucrose	1, 2, 3, 4, 5, 6
Salicylic acid	1, 2, 3, 4, 5, 6	Sulphanilic acid	1, 2, 3, 4, 5, 6
Starch, soluble	1, 3, 4, 5, 6	Sulphosalicylic acid	1, 6
Succinic acid	1, 2, 3, 4, 5, 6		
Tartaric acid	1, 2, 3, 4, 5, 6	Toluene	2, 3, 4, 5, 6
Tannic acid	2, 3, 4, 5, 6	Trichloroacetic acid	1, 2, 3, 4, 5, 6
Thiourea	5	Thymol blue	6
Thymol	5		
Urea	2, 3, 4, 5, 6	Uric acid	5
Vanillin	1	*iso*-Valeric acid	5
Xylene	2, 3, 4, 5, 6		

A, 10. BUFFER SOLUTIONS

1. *Buffers suitable for precision standardisation of* p*H measurements* (*D. A. MacInnes, 1939*)

	12°C	*25°C*	*38°C*
	p*H*	p*H*	p*H*
CH_3COOH (0·01*N*), CH_3COONa (0·01*N*)	4·710	4·700	4·710
CH_3COOH (0·1*N*), CH_3COONa (0·1*N*)	4·650	4·640	4·635
Potassium acid phthalate (0·05*M*)	4·000	4·000	4·015

2. p*H Range : 0·65 to 5·20 ; 18°C* (*Walpole, 1914*)

50 Ml. N-*Sodium acetate* + *X ml.* N-*HCl made up to 250 ml.*

p*H*	*X* (ml.) HCl	p*H*	*X* (ml.) HCl	p*H*	*X* (ml.) HCl
0·65	100	1·99	52·5	3·79	42·5
0·75	90	2·32	51·0	3·95	40·0
0·91	80	2·64	50·0	4·19	35·0
1·09	70	2·72	49·75	4·39	30·0
1·24	65	3·09	48·5	4·58	25·0
1·42	60	3·29	47·5	4·76	20·0
1·71	55	3·49	46·25	4·92	15·0
1·85	53·5	3·61	45·0	5·20	10·0

3. p*H Range : 3·42 to 5·89 ; 18°C* (*Walpole, 1914*)

*10 Ml. mixtures of X ml. of 0·2N acetic acid and Y ml. of 0·2*N *sodium acetate.*

X (ml.)	*Y* (ml.)	p*H*	*X* (ml.)	*Y* (*ml.*)	p*H*
9·5	0·5	3·42	4·0	6·0	4·80
9·0	1·0	3·72	3·0	7·0	4·99
8·0	2·0	4·05	2·0	8·0	5·23
7·0	3·0	4·27	1·5	8·5	5·37
6·0	4·0	4·45	1·0	9·0	5·57
5·0	5·0	4·63	0·5	9·5	5·89

4. pH Range: 2·2 to 8·0 (*McIlvaine, 1921*)

20 Ml. mixtures of X ml. of 0·2M Na_2HPO_4 and Y ml. of 0·1M citric acid.

X (ml.) Na_2HPO_4	*Y* (ml.) Citric acid	p*H*	*X*(ml.) Na_2HPO_4	*Y* (ml.) Citric acid	p*H*
0·40	19·60	2·2	10·72	9·28	5·2
1·24	18·76	2·4	11·15	8·85	5·4
2·18	17·82	2·6	11·60	8·40	5·6
3·17	16·83	2·8	12·09	7·91	5·8
4·11	15·89	3·0	12·63	7·37	6·0
4·94	15·06	3·2	13·22	6·78	6·2
5·70	14·30	3·4	13·85	6·15	6·4
6·44	13·56	3·6	14·55	5·45	6·6
7·10	12·90	3·8	15·45	4·55	6·8
7·71	12·29	4·0	16·47	3·53	7·0
8·28	11·72	4·2	17·39	2·61	7·2
8·82	11·18	4·4	18·17	1·83	7·4
9·35	10·65	4·6	18·73	1·27	7·6
9·86	10·14	4·8	19·15	0·85	7·8
10·30	9·70	5·0	19·45	0·55	8·0

5. pH Range: 5·29 to 8·04; 18°C (*Sörensen, 1909–12*)

10 Ml. mixtures of X ml. M/15 Na_2HPO_4 and Y ml. of M/15 KH_2PO_4.

X (ml.) $NaHPO_4$	*Y* (ml.) KH_2PO_4	p*H*	*X* (ml.) Na_2HPO_4	*Y* (ml.) KH_2PO_4	p*H*
0·25	9·75	5·29	5·0	5·0	6·81
0·5	9·5	5·59	6·0	4·0	6·98
1·0	9·0	5·91	7·0	3·0	7·17
2·0	8·0	6·24	8·0	2·0	7·38
3·0	7·0	6·47	9·0	1·0	7·73
4·0	6·0	6·64	9·5	0·5	8·04

6. p*H* Ranges : 2·2 to 3·8, 4·0 to 6·2, 5·8 to 8·0, 7·8 to 10·0 ; 20°C (*Clark and Lubs, 1916*)

(*A*) *p*H 2·2–3·8. *50 Ml. 0·2*M *K H Phthalate + P ml. 0·2*M *HCl, diluted to 200 ml.*

(*B*) *p*H 4·0–6·2. *50 Ml. 0·2*M *K H Phthalate + Q ml. 0·2*M *NaOH, diluted to 200 ml.*

(*C*) *p*H 5·8–8·0. *50 Ml. 0·2*M KH_2PO_4 + *R ml. 0·2* M *NaOH, diluted to 200 ml.*

(*D*) *p*H 7·8–10·0. *50 Ml. 0·2*M H_3BO_3 *and 0·2*M *KCl** + *S ml. 0·2*M *NaOH, diluted to 200 ml.*

A		*B*		*C*		*D*	
P (ml.) HCl	*p*H	*Q* (ml.) NaOH	*p*H	*R* (ml.) NaOH	*p*H	*S* (ml.) NaOH	*p*H
46·60	2·2	0·40	4·0	3·66	5·8	2·65	7·8
39·60	2·4	3·65	4·2	5·64	6·0	4·00	8·0
33·00	2·6	7·35	4·4	8·55	6·2	5·90	8·2
26·50	2·8	12·00	4·6	12·60	6·4	8·55	8·4
20·40	3·0	17·50	4·8	17·74	6·6	12·00	8·6
14·80	3·2	23·65	5·0	23·60	6·8	16·40	8·8
9·95	3·4	29·75	5·2	29·54	7·0	21·40	9·0
6·00	3·6	35·25	5·4	34·90	7·2	26·70	9·2
2·65	3·8	39·70	5·6	39·34	7·4	32·00	9·4
—	—	43·10	5·8	42·74	7·6	36·85	9·6
—	—	45·40	6·0	45·17	7·8	40·80	9·8
—	—	47·00	6·2	46·85	8·0	43·90	10·0

7. p*H* Range : 6·80 to 9·60 ; 25°C (*Michaelis, 1930*)

*10 Ml. mixtures of X ml. of 0·1*M *sodium diethylbarbiturate and Y ml. of 0·1*M *HCl.*

X (*ml.*) Na salt	*Y* (ml.) HCl	*p*H	*X* (ml.) Na salt	*Y* (ml.) HCl	*p*H
5·22	4·78	6·80	8·23	1·77	8·40
5·36	4·64	7·00	8·71	1·29	8·60
5·54	4·46	7·20	9·08	0·92	8·80
5·81	4·19	7·40	9·36	0·64	9·00
6·15	3·85	7·60	9·52	0·48	9·20
6·62	3·38	7·80	9·74	0·26	9·40
7·16	2·84	8·00	9·85	0·15	9·60

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* That is, a solution containing 12·369 g. of H_3BO_3 and 14·911 g. of KCl per litre.

8. *p*H Range: 8·45 to 12·77; 24°C (*Sörensen-Walbum, 1920*)

*10 Ml. mixtures of X ml. of 0·1*M *glycine + 0·1*M *NaCl* and Y ml. of 0·1*M *NaOH.*

X (ml.) Glycine -NaCl	*Y* (ml.) NaOH	*p*H	*X* (ml.) Glycine -NaCl	*Y* (ml.) NaOH	*p*H
9·5	0·5	8·45	5·0	5·0	11·14
9·0	1·0	8·79	4·9	5·1	11·39
8·0	2·0	9·22	4·5	5·5	11·92
7·0	3·0	9·56	4·0	6·0	12·21
6·0	4·0	9·98	3·0	7·0	12·48
5·5	4·5	10·32	2·0	8·0	12·66
5·1	4·9	10·90	1·0	9·0	12·77

9. *p*H Ranges: 1·40 to 2·20, 2·30 to 3·30, 2·90 to 4·10, 3·40 to 5·20, 4·80 to 6·20; 25°C (*German and Vogel, 1937*)

*X Ml. of 0·1*M *para-toluenesulphonic acid monohydrate (19·012 g. per litre) and Y ml. of 0·1*M *sodium para-toluenesulphonate (19·406 g. per litre), diluted to 100·0 ml.*

X (ml.)	*Y* (ml.)	*p*H	*X* (ml.)	*Y* (ml.)	*p*H
48·9	1·1	1·40	36·8	13·2	1·90
37·2	12·8	1·50	40·0	10·0	2·00
27·4	22·6	1·60	42·4	7·6	2·10
19·0	31·0	1·70	45·6	4·4	2·20
16·6	33·4	1·80			

*X Ml. of 0·01*M *para-toluenesulphonic acid monohydrate (1·9012 g. per litre) and Y ml. of 0·01*M *sodium para-toluenesulphonate (1·9046 g. per litre), diluted to 100·0 ml.*

X (ml.)	*Y* (ml.)	*p*H	*X* (ml.)	*Y* (ml.)	*p*H
50·0	0·0	2·30	12·4	37·6	2·90
44·2	5·8	2·40	10·0	40·0	3·00
35·8	14·2	2·50	8·0	42·0	3·10
27·6	22·4	2·60	6·2	43·8	3·20
21·2	28·8	2·70	5·0	45·0	3·30
18·5	31·5	2·80			

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* That is, a solution containing 7·505 g. of glycerine + 5·85 g. of NaCl per litre.

*X Ml. of 0·01*M *furoic acid (1·1203 g. per litre) and Y ml. of 0·01*M *sodium furoate (1·3403 g. per litre) diluted to 100·0 ml.*

X (ml.)	*Y* (ml.)	*p*H	*X* (ml.)	*Y* (ml.)	*p*H
45·2	4·8	2·90	14·8	35·2	3·60
39·6	10·4	3·00	12·3	37·7	3·70
34·0	16·0	3·10	10·1	39·9	3·80
28·4	21·6	3·20	8·4	41·6	3·90
24·8	25·2	3·30	6·7	43·3	4·00
21·4	28·6	3·40	5·4	44·6	4·10
18·0	32·0	3·50			

*X Ml. of 0·01*M *phenylacetic acid (1·3606 g. per litre) and Y ml. of 0·01*M *sodium phenylacetate (1·5806 g. per litre), diluted to 100·0 ml.*

X (ml.)	*Y* (ml.)	*p*H	*X* (ml.)	*Y* (ml.)	*p*H
48·7	1·3	3·40	22·0	28·0	4·40
46·6	3·4	3·50	19·4	30·6	4·50
44·4	5·6	3·60	16·9	33·1	4·60
42·2	7·8	3·70	14·4	35·6	4·70
39·9	10·1	3·80	12·1	37·9	4·80
37·2	12·6	3·90	10·2	39·8	4·90
34·4	15·6	4·00	8·6	41·4	5·00
30·8	19·2	4·10	7·2	42·8	5·10
28·0	22·0	4·20	5·7	44·3	5·20
25·1	24·9	4·30			

*X Ml. of 0·01*M *sodium hydrogen succinate (0·5903 g. of succinic acid + 0·8102 g. of disodium succinate per litre) and Y ml. of 0·01*M *disodium succinate (1·6203 g. per litre), diluted to 100·0 ml.*

X (ml.)	*Y* (ml.)	*p*H	*X* (ml.)	*Y* (ml.)	*p*H
48·8	1·2	4·80	21·0	29·0	5·60
46·9	3·1	4·90	17·6	32·4	5·70
44·4	5·6	5·00	14·7	35·3	5·80
40·4	9·6	5·10	12·0	38·0	5·90
36·2	13·8	5·20	9·9	40·1	6·00
32·6	17·4	5·30	7·8	42·2	6·10
28·6	21·4	5·40	5·6	44·4	6·20
24·7	25·3	5·50			

A, 11. COMPARISON OF METRIC AND OTHER UNITS

Metric system.—The primary unit of **length** is the **metre,** which is the distance between two lines, under standard conditions, engraved on a prototype preserved in the Bureau International des Poids et Mesures, Sèvres, France.

The primary unit of **weight** is the **kilogram,** which is the mass of a prototype preserved in the same place.

The primary unit of **volume** is the **litre,** and is the volume occupied by one kilogram of pure water at 4°C under a pressure of 760 mm. of mercury (see, however, Section **II, 17**).

The **millilitre** (ml.) is the thousandth part of a litre. One millilitre is nearly, but not absolutely equal to cubic centimetre (c.c.) :

1000 ml. = 1000·027 c.c.

UNITS OF LENGTH

1 millimetre (mm.) = 0·03937 inch.
1 centimetre (cm.) = 0·3937 inch.
1 metre (m.) = 39·370 inches.
1 metre = 3·2808 feet.
1 kilometre (km.) = 1093·61 yards.
1 kilometre = 0·62137 mile.

1 inch (in.) = 25·400 millimetres.
1 inch = 2·5400 centimetres.
1 foot (ft.) = 304·801 millimetres.
1 foot = 0·30480 metre.
1 yard (yd.) = 0·91440 metre.
1 mile = 1·60934 metres.

UNITS OF AREA

1 square mm. = 0·001550 sq. in.
1 square cm. = 0·1550 sq. in.
1 square metre = 1550·0 sq. ins.
1 square metre = 10·7638 sq. ft.
1 square metre = 1·1960 sq. yds.
1 square km. = 0·38610 sq. mile.
1 hectare = 2·4710 acres.

1 square in. = 645·16 sq. mm.
1 square in. = 6·4516 sq. cm.
1 square ft. = 929·03 sq. cm.
1 square ft. = 0·9290 sq. m.
1 square yd. = 0·86313 sq. m.
1 acre = 0·40469 hectare.
1 square mile = 2·5900 sq. km.

UNITS OF VOLUME

1 cubic mm. = 0·00006102 cubic in.
1 cubic cm. (c.c. or ml.) = 0·061024 cubic in.
1 cubic m. = 61,024 cubic ins.
1 cubic m. = 35·3144 cubic ft.
= 1·3079 cubic yds.

1 cubic in. = 16,387 cubic mm.
1 cubic in. = 16·387 ml.
1 cubic ft. = 0·028317 cubic m.
1 cubic ft. = 28·317 litres.
1 cubic yd. = 0·7645 cubic m.

MEASURES OF LIQUID CAPACITY

Imperial or British Units

1 gill = 142·06 ml.
1 pint = 4 gills = 568·25 ml.
1 quart = 2 pints = 1·13649 litres.
1 gallon = 4 quarts = 4·54596 litres.

Apothecaries' Units (British)

1 minim = 0·059192 ml.
1 fluid scruple = 20 minims = 1·1838 ml.
1 fluid drachm = 3 scruples = 3·5515 ml.
1 fluid ounce = 8 fluid drachms = 28·412 ml.
1 pint = 20 fluid ounces = 568·25 ml.
1 gallon = 8 pints = 4·54596 litres.

U.S. Units.

1 gill = 118·292 ml.
1 pint = 4 gills = 473·167 ml.
1 quart = 2 pints = 0·94633 litre.
1 gallon = 4 quarts = 3·78533 litres.

Apothecaries. Units (U.S.)

1 minim = 0·06161 ml.
1 fluid drachm = 60 minims = 3·69661 ml.
1 fluid ounce = 8 fluid drachms = 29·5729 ml.
1 pint = 16 fluid ounces = 473·167 ml.
1 gallon = 8 pints = 3·78533 litres.

UNITS OF MASS

Avoirdupois Weight

1 grain = 64·799 mg.
1 dram = 27·3437 grains = 1·77185 g.
1 ounce = 16 drams = 437·5 grains = 28·34954 g.
1 pound = 16 ounces = 7000 grains = 453·5926 g.
1 stone = 14 pounds = 6·35030 kg.
1 quarter = 28 pounds = 12·70059 kg.
1 hundredweight = 112 pounds = 50·80238 kg.

1 gram = 15·4325 grains.
1 decagram = 10 grams = 5·64383 drams.
1 hectogram = 100 grams = 3·52739 ounces.
1 kilogram = 1000 grams = 2·204621 pounds.
1 myriagram = 10 kilograms = 22·04621 pounds.
1 quintal = 100 kilograms = 1·98641 hundredweights.
1 millier = 1 metric ton = 1000 kilograms = 0·9842059 ton.

Troy Weight

1 grain = 64·799 mg.
1 pennyweight (dwt) = 24 grains = 1·29598 g.
1 ounce = 20 pennyweights = 480 grains = 31·1035 g.
1 pound = 12 ounces = 373·2418 g.

Apothecaries' Weight

1 grain = 64·799 mg.
1 scruple = 20 grains = 1·29598 g.
1 drachm = 3 scruples = 3·88794 g.
1 ounce = 8 drachms = 480 grains = 31·1035 g.
1 pound = 12 ounces = 373·2418 g.

A, 12. DECIMALS OF AN INCH, I.S.W.G., AND MILLIMETRES

Decimals of an inch	*I.S.W.G.*	*Milli-metres*	*Decimals of an inch*	*I.S.W.G.*	*Milli-metres*
0·400	0000	10·160	0·040	19	1·016
0·372	000	9·449	0·036	20	0·914
0·348	00	8·839	0·032	21	0·813
0·324	0	8·230	0·028	22	0·711
0·300	1	7·620	0·024	23	0·610
0·276	2	7·010	0·022	24	0·559
0·252	3	6·401	0·020	25	0·508
0·232	4	5·893	0·018	26	0·457
0·212	5	5·385	0·016	27	0·416
0·192	6	4·877	0·015	28	0·376
0·176	7	4·470	0·014	29	0·345
0·160	8	4·064	0·012 +	30	0·315
0·144	9	3·658	0·012 −	31	0·295
0·128	10	3·251	0·011	32	0·274
0·116	11	2·946	0·010	33	0·254
0·104	12	2·642	0·009	34	0·233
0·092	13	2·337	0·008 +	35	0·213
0·080	14	2·032	0·008 −	36	0·193
0·072	15	1·829	0·007	37	0·172
0·064	16	1·626	0·006	38	0·152
0·056	17	1·422	0·005 +	39	0·132
0·048	18	1·219	0·005 −	40	0·122

A, 13. THE GREEK ALPHABET

Greek Letter		*Greek Name*	*English Equivalent*	*Greek Letter*		*Greek Name*	*English Equivalent*
Α	α	Alpha	a	*Ν*	ν	Nu	n
Β	β	Beta	b	*Ξ*	ξ	Xi	x
Γ	γ	Gamma	g	*Ο*	ο	Omicron	ŏ
Δ	δ	Delta	d	*Π*	π	Pi	p
Ε	ϵ	Epsilon	ĕ	*Ρ*	ρ	Rho	r
Ζ	ζ	Zeta	z	*Σ*	σ	Sigma	s
Η	η	Eta	ē	*Τ*	τ	Tau	t
Θ	θ	Theta	th	*Υ*	υ	Upsilon	u
Ι	ι	Iota	i	*Φ*	ϕ	Phi	ph
Κ	κ	Kappa	k	*Χ*	χ	Chi	ch
Λ	λ	Lambda	l	*Ψ*	ψ	Psi	ps
Μ	μ	Mu	m	*Ω*	ω	Omega	ō

A,14. SUGGESTED SCHEME OF STUDY FOR INTERMEDIATE SCIENCE AND ENGINEERING, HIGHER SCHOOL CERTIFICATE AND ORDINARY NATIONAL CERTIFICATE EXAMINATIONS IN CHEMISTRY, AND EXAMINATIONS OF SIMILAR CHARACTER

The following scheme is suggested as suitable for a course of training in quantitative analysis for beginners. It covers the requirements of the intermediate examination in science and engineering, the higher school certificate examination, the first medical examination, the ordinary national certificate in chemistry, and examinations of similar scope. Experiments marked with an asterisk are optional.

Acidimetry and Alkalimetry

(i) Preparation of approx. 0·1*N* hydrochloric acid (Section **III, 4**) and standardisation against (*a*) anhydrous sodium carbonate (method of Note 1 in Section **III, 4A**) or (*b*) borax (method of Note 1 in Section **III, 4B**).

(ii) Preparation of approx. 0·1*N* sodium hydroxide solution (Section **III, 5** ; *Procedure A*) and standardisation against (*a*) *ca.* 0·1*N* hydrochloric acid (Section **III, 6** ; *Procedure A*) or (*b*) potassium hydrogen phthalate (Section **III, 6** ; *Procedure B*).

(iii) Determination of Na_2CO_3 in washing soda with standard hydrochloric acid (Section **III, 9**).

(iv) Determination of strength of glacial acetic acid with standard sodium hydroxide solution (Section **III, 10**).

(v) *Determination of H_2SO_4 in the concentrated acid with standard sodium hydroxide solution (Section **III, 11**).

(vi) Analysis of commercial caustic soda (mixture of hydroxide and carbonate (Section **III, 14** ; *Procedure B*).

(vii) Determination of $Na_2B_4O_7$ in borax (Section **III, 17** ; titration with standard acid and indicator only).

(viii) Determination of NH_3 in ammonium chloride (Section **III, 18** ; indicator method).

Determinations with Potassium Permanganate Solution

(i) Preparation of 0·1*N* potassium permanganate (Section **III, 47**).

(ii) Standardisation of the potassium permanganate solution (*a*) with arsenious oxide, (Section **III, 48A** ; Note 1), (*b*) with sodium oxalate (Section **III, 48B** ; Note 1).

(iii) Determination of iron in crystallised ferrous sulphate (Section **III, 50**).

(iv) Determination of iron in ferric ammonium sulphate (Section **III, 52** ; reduction with stannous chloride as in Section **III, 51A**).

(v) *Determination of total iron in an iron ore (Section **III, 53** ; reduction with stannous chloride as in Section **III, 51A**).

(vi) Determination of H_2O_2 in the commercial solution (Section **III, 55**).

(vii) Determination of calcium in calcium carbonate (Section **III, 54**).

(viii) Determination of MnO_2 in pyrolusite (Section **III, 57** ; *Procedure B*).

(ix) *Determination of KNO_2 in commercial potassium nitrite (Section **III. 58**).

Determinations with Potassium Dichromate Solution

(i) Preparation of 0·1*N* potassium dichromate (Section **III, 64**).

(ii) Check standardisation of potassium dichromate solution against pure iron (Section **III, 65**).

(iii) Determination of iron in crystallised ferrous sulphate or ferrous ammonium sulphate (Section **III, 66**) ; sodium diphenylamine sulphonate or *N*-phenylanthranilic acid as indicator.

(iv) Determination of iron in ferric ammonium sulphate (Section **III, 67**).

(v) *Determination of total iron in an iron ore (Section **III, 68**).

(vi) *Determination of chromium in chrome alum (Section **III, 70**).

Iodimetry and Iodometry

(i) Preparation of approx. $0{\cdot}1N$ sodium thiosulphate solution (Section **III, 101**).

(ii) Standardisation of the thiosulphate solution against (*a*) standard potassium iodate solution (Section **III, 102A** ; Note 1), (*b*) standard potassium dichromate solution (Section **III, 102D**).

(iii) Preparation of approx. $0{\cdot}1N$ iodine solution (Section **III, 103** ; *Method A*).

(iv) Standardisation of the iodine solution against (*a*) pure arsenious oxide (Section **III, 104A**), (*b*) standard sodium thiosulphate solution (Section **III, 104B**).

(v) Determination of copper in crystallised copper sulphate (Section **III, 105** ; *Method A*).

(vi) Determination of MnO_2 in pyrolusite (Section **III, 107**).

(vii) Determination of H_2O_2 in the commercial solution (Section **III, 110**).

(viii) Determination of available chlorine in bleaching powder : (*a*) iodometric method (Section **III, 111** ; *Procedure A*), (*b*) arsenite method (Section **III, 111** ; *Procedure* B).

(ix) Determination of antimony in tartar emetic (Section **III, 113**).

(x) *Determination of tin in crystallised stannous chloride (Section **III, 116** ; *Procedure A*).

(xi) *Determination of purity of crystallised sodium sulphite (Section **III, 118**).

(xii) *Determination of H_2S in aqueous solution (Section **III, 119**).

Precipitation Reactions

Use of Standard Solutions of Silver Nitrate and of Ammonium Thiocyanate

(i) Preparation of approx. $0{\cdot}1N$ silver nitrate solution (Section **III, 22** ; *Procedure B*).

(ii) Standardisation of the silver nitrate solution against standard sodium chloride solution (*a*) with potassium chromate as indicator—Mohr's method (Section **III, 23A**), (*b*) with fluorescein as indicator—Fajan's method (Section **III, 23B**).

(iii) *Analysis of a mixture of potassium chloride and bromide (Section **III, 30**).

(iv) Preparation of approx. $0{\cdot}1N$ sodium thiosulphate solution (Section **III, 31**).

(v) Standardisation of the ammonium thiocyanate solution against standard silver nitrate solution by Volhard's method (Section **III, 31**).

(vi) *Determination of silver in a silver alloy (Section **III, 32**).

(vii) Determination of the HCl content of concentrated hydrochloric acid (Section **III, 33**).

(viii) *Determination of KCN in commercial potassium cyanide (Section **III, 41** ; *Procedure A*).

Simple Gravimetric Analysis

(i) *Determination of water of crystallisation in crystallised barium chloride (Section **IV, 4**).

(ii) *Determination of chlorine in sodium chloride (Section **IV, 5**).

(iii) *Determination of sulphate in potassium sulphate (Section **IV, 6**).

(iv) *Determination of iron in ferrous ammonium sulphate (Section **IV, 7**).

A, 15. SUGGESTED SCHEME OF STUDY FOR B.Sc. SPECIAL CHEMISTRY, HONOURS B.Sc. CHEMISTRY, ASSOCIATESHIP OF THE INSTITUTE OF CHEMISTRY, AND EXAMINATIONS OF SIMILAR SCOPE

The scheme given below is proposed as a basis for a course in quantitative analysis for advanced courses in chemistry. The experiments marked with an asterisk are of more difficult character ; they are suitable for A.I.C. students and may be omitted, if desired, by B.Sc. honours students. It is not expected that any one student will be able to carry out all the determinations listed below, but a sufficient number is given to allow a choice at the discretion of the teacher. It need hardly be stated that many teachers will prefer to adopt their own courses, and it is believed that details of most of the necessary determinations will be found in the book.

VOLUMETRIC ANALYSIS

Acidimetry and Alkalimetry

(i) Calibration of weights (Section **II, 8**).

(ii) Calibration of volumetric apparatus :
  (*a*) volumetric flasks, 250 ml., 500 ml., 1000 ml. (Section **II, 20**) ;
  (*b*) pipettes, 10 ml., 25 ml., 50 ml. (Section **II, 21**) ;
  (*c*) burette (Section **II, 22**).

(iii) Preparation of 0·1*N* hydrochloric acid (Section **III, 3** or **III, 4**). Standardisation against :
  (*a*) borax (Section **III, 4B**) ;
  (*b*) anhydrous sodium carbonate (Section **III, 4A**).

(iv) Determination of SO_3 in oleum (Section **III, 12**).

(v) Determination of NH_3 in an ammonium salt (Section **III, 18** ; direct method) *or* of $NaNO_3$ in Chili saltpetre (Section **III, 19**).

(vi) Determination of nitrogen by Kjeldahl's method (Section **III, 20**).

Precipitation and Complex-Formation Reactions

(i) Preparation and standardisation of 0·1*N* silver nitrate (Sections **III, 22** and **III, 23**).

(ii) *Determination of chloride and iodide or of bromide and iodide in admixture (Section **III, 29**).

(iii) Preparation and standardisation of 0·1*N* ammonium thiocyanate (Section **III, 31**).

(iv) Analysis of a hyposulphite (Section **III, 36**).

(v) Determination of cyanide in potassium cyanide (Section **III, 41**).

(vi) Determination of nickel :
  (*a*) with pyridine and standard ammonium thiocyanate (Section **III, 38**);
  (*b*) with potassium cyanide solution (Section **III, 42**).

Oxidations with Potassium Permanganate

(i) Preparation of 0·1*N* potassium permanganate and standardisation against :
  (*a*) arsenious oxide (Section **III, 48A**) ;
  (*b*) sodium oxalate (Section **III, 48B**).

(ii) Determination of total iron in an iron ore (Section **III, 53** ; reduction with (*a*) stannous chloride and (*b*) the Jones' reductor—Section **III, 51**).

(iii) Analysis of sodium peroxide (Section **III, 56**).

(iv) Determination of MnO_2 in pyrolusite (Section **III, 57**).

(v) Determination of a nitrite (Section **III, 58**).

(vi) Determination of a persulphate (Section **III, 59**).

(vii) Determination of manganese in steel by the bismuthate method (Section **III, 60**).

Oxidations with Potassium Dichromate

(i) Preparation of 0·1*N* potassium dichromate (Section **III, 64**).

(ii) Determination of ferrous and ferric iron in an iron ore (Section **III, 69**).

(iii) Determination of chromium in chromite (Section **III, 71**).

Oxidations with Ceric Sulphate

(i) Preparation of approx. $0{\cdot}1N$ ceric sulphate solution (Section **III, 74**) and standardisation against :
  (*a*) arsenious oxide (Section **III, 75A**) ;
  (*b*) pure iron (Section **III, 75B**).
(ii) Determination of an oxalate (Section **III, 76**).
(iii) Determination of iron in an iron ore (Section **III, 77**).
(iv) Determination of a ferrocyanide (Section **III, 78**).
(v) Determination of a nitrite (Section **III, 79**).

Reductions with Titanous Sulphate

(i) *Preparation of titanous sulphate solution (Section **III, 87B**) and standardisation against pure iron (Section **III, 88A**).
(ii) *Determination of iron in an iron ore (Section **III, 89**).

IODIMETRY AND IODOMETRY

Determinations with Sodium Thiosulphate

(i) Preparation of $0{\cdot}1N$ sodium thiosulphate (Section **III, 101**) and standardisation against :
  (*a*) potassium iodate (Section **III, 102A**) ;
  (*b*) potassium dichromate (Section **III, 102D**) ;
  (*c*) pure copper (Section **III, 102E**).
(ii) Preparation of $0{\cdot}1N$ iodine (Section **III, 103**) and standardisation. against :
  (*a*) arsenious oxide (Section **III, 104A**) ;
  (*b*) $0{\cdot}1N$ sodium thiosulphate (Section **III, 104B**).
(iii) Determination of copper in an ore (Section **III, 106**).
(iv) Determination of manganese dioxide in pyrolusite (Section **III, 107**).
(v) Determination of available chlorine in bleaching powder (Section **III, 111**).
(vi) Determination of a chlorate or a bromate (Section **III, 108**).
(vii) *Determination of tin in an alloy (Section **III, 116A**).
(viii) *Determination of antimony and tin in type metal (Section **III, 117**).
(ix) Determination of a sulphite (Section **III, 118**).

Oxidations with Potassium Iodate

(i) Preparation of $0{\cdot}1N$ (or $0{\cdot}025M$) potassium iodate (Section **III, 123**).
(ii) Determination of an iodide (Section **III, 124**).
(iii) Determination of arsenic or of antimony (Section **III, 125**).
(iv) Determination of copper (Section **III, 126**).
(v) *Determination of tin (Section **III, 128**).
(vi) Determination of hydrogen peroxide (Section **III, 129**).

Oxidations with Potassium Bromate

(i) Preparation of $0{\cdot}1N$ potassium bromate (Section **III, 136**).
(ii) Determination of antimony or of arsenic (Section **III, 137**).
(iii) Determination of aluminium or of magnesium by the oxine method (Section **III, 136** ; *Procedure A and B*).

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(i) Determination of chloride as AgCl (Section **IV, 5**).
(ii) Determination of sulphate as $BaSO_4$ (Section **IV, 6**).
(iii) *Determination of sulphur in iron pyrites (Section **IV, 7**).
(v) Determination of iron as Fe_2O_3 (Section **IV, 8**).
(v) Determination of aluminium as Al_2O_3 (Section **IV, 9**).
(vi) Determination of calcium as $CaCO_3$ or as CaO (Section **IV, 10**).

(vii) Determination of magnesium as $Mg_2P_2O_7$ (Section **IV, 11**).
(viii) Determination of nickel with dimethylglyoxime (Section **IV, 12**).
(ix) Determination of lead as $PbCrO_4$ or as $PbSO_4$ (Section **IV, 14**).
(x) Determination of mercury as HgS or as $Hg[Zn(CNS)_4]$ (Section **IV, 16**).
(xi) *Determination of bismuth as BiOI (Section **IV, 17**).
(xii) *Determination of cadmium by the pyridine method (Section **IV, 18**).
(xiii) Determination of copper as $Cu_2(CNS)_2$ (Section **IV, 19**).
(xiv) *Determination of tin as SnO_2 (Section **IV, 22**).
(xv) Determination of aluminium as the 8-hydroxy-quinolate (Section **IV, 28**).
(xvi) Determination of chromium by the cyanate method or by the mercurous chromate method (Section **IV, 30**).
(xvii) Determination of iron with cupferron (Section **IV, 31**).
(xviii) Determination of cobalt with α-nitroso-β-naphthol (Section **IV, 33**).
(xix) Determination of zinc as $ZnNH_4PO_4$ and/or $Zn_2P_2O_7$ (Section **IV, 34**).
(xx) Determination of sodium as sodium zinc uranyl acetate (Section **IV, 47**).
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(xxii) *Determination of fluorine as PbClF (Section **IV, 57**).
(xxiii) Determination of phosphorus as $Mg_2P_2O_7$ (Section **IV, 65**).
(xxiv) Determination of silica in a soluble silicate and in an insoluble silicate (Section **IV, 70**).
(xxv) Determination of a carbonate (Section **IV, 76**).

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(iii) Determination of nickel (Section **IV, 81**).
(iv)* Determination of zinc (Section **IV, 84**).

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(i) Iron and aluminium (Section **IV, 86A**).
(ii) Iron and chromium (Section **IV, 86B**).
(iii) Nickel and zinc (Section **IV, 86D**).
(iv) Calcium and magnesium (Section **IV, 86E**)
(v) Calcium and barium (Section **IV, 86F**).
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(ii) *Determination of iron by the thiocyanate method (Section **V, 10A**).
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(iv) *Determination of titanium by the hydrogen peroxide method (Section **V, 12**).
(v) *Determination of chromium with diphenylcarbazide (Section **V, 14**).
(vi) *Determination of lead by the dithizone method (Section **V, 22**).
(vii) *Determination of copper by the ferrocyanide method and/or the sodium diethyldithiocarbamate method (Section **V, 23**).
(viii) *Determination of silicate by the molybdate method (Section **V, 26**).

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(iii) *Analysis of coal gas with the Orsat apparatus (Section **VI, 6C**).
(iv) *Analysis of coal gas with the Ambler apparatus (Section **VI, 6D**).
(v) *Determination of a nitrate with the Lunge nitrometer (Section **VI, 11**).
(vi) *Evaluation of pyrolusite (Section **VI, 13**).
(vii) *Determination of available chlorine in bleaching powder (Section **VI, 14**).
(viii) *Determination of ammonia in an ammonium salt (Section **VI, 16**).

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											MEAN DIFFERENCES								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6848	6848	6857	6866	6875	6884	6893	1	2	3	4	5	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

FOUR-FIGURE LOGARITHMS

											MEAN DIFFERENCES								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	4774	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

A, 17. FIVE-FIGURE LOGARITHMS*

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INDEX

The following abbreviations are used :—

D. = determination
v = volumetric
g = gravimetric
c = colorimetric
e = electrolytic
gv = gas-volumetric

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